SURFACE TENSION
AND
SURFACE ENERGY

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SURFACE TENSION AND SURFACE ENERGY AND THEIR INFLUENCE ON CHEMICAL PHENOMENA

BY

R. S. WILLOWS, M.A., D.Sc., AND E. HATSCHEK

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PREFACE

The present small book is based on a course of lectures delivered at the Sir John Cass Technical Institute by one of the authors, in response to the wishes of a number of students who had attended the course on colloids.

The object of the work is to give the student of chemistry an adequate idea of the fundamental laws of surface tension and surface energy while avoiding the purely mathematical exercises which occupy so much of the space devoted to the subject in text-books of physics, and then to deal at some length with the relations between surface energy and such constants and phenomena as are likely to be of interest to the chemist and biologist. The mathematical treatment has been confined to what is absolutely essential, and generally the aim has been to give established facts or hypotheses which have proved their value rather than to apply them to special cases of limited interest. As our chief object has been to expose the physical principles involved, few experimental details have been given except for the most recent investigations.

It is hoped that the book may prove useful to those engaged in the study of chemistry, and more particularly of colloidal chemistry, either from its biological or from its purely chemical aspect.

R. S. WILLOWS.
E. HATSCHEK.

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SURFACE TENSION AND SURFACE ENERGY

AND THEIR INFLUENCE ON CHEMICAL PHENOMENA.

CHAPTER I.

Among the purely physical properties of their materials, to which the chemist and the biologist have been compelled to pay an increasing amount of attention during recent years, surface tension undoubtedly occupies the first place. In a great measure this is due to the development of colloidal chemistry, which deals with matter in a state of extreme sub-division, and therefore with a great development of surface for a given mass, so that the properties of surfaces become important, and sometimes decisive, factors in the behaviour of such systems.

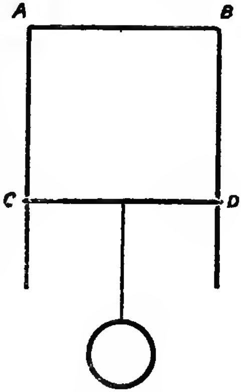

Fig. 1.

Everybody is familiar with a number of phenomena which indicate that the surface of a liquid is in a condition of tension, or—to use a parallel which is graphic, while incorrect in one particular—behaves as if it were composed of an elastic membrane. If a camel-hair brush is submerged in water, the hairs remain separate as they do in air, but they collapse on being withdrawn, *i.e.*, the surface of the adhering water behaves like an elastic sheath, tending to contract. Drops of liquid not exposed to external forces, that is, either falling freely or suspended in another liquid of the same density, assume a spherical shape, the sphere being the body with the minimum surface for a given volume.

While these phenomena demonstrate beyond doubt the existence of a surface tension at the surface of a liquid bounded by air or, strictly speaking, its own vapour, we can obtain a much clearer view of its action by considering an arrangement first suggested by Maxwell. Imagine a rectangular wire frame AB (Fig. 1) on which a movable wire CD slides parallel with AB. If we fill the rectangle ABCD with a film of liquid, this will contract and raise the wire CD. If we now weight the latter, we can find a weight which will just stretch the liquid film—within certain limits—indefinitely. Bearing in mind that the film as here described has two surfaces, we find that this weight gives us the double surface tension exerted by the width CD, and if we divide half the weight by this width, we obtain the *surface tension per unit length,* which is the form in which this constant is usually given. The units employed are either milligrammes per millimetre, or, more generally, absolute units, viz., dynes per centimetre. (The dyne is the force which imparts an acceleration of one centimetre per second to the mass of a gramme; it is accordingly gm./980, or approximately equal to a milligramme weight.) It is easy to see that values given in mgm./mm. are transformed into dyne/cm. measure through multiplication by the factor 9·8.

The possibility of stretching the film indefinitely shows the important fact that the *surface tension per unit length is independent of the size of the surface,* and this constitutes the difference between the surface tension and the tension of an elastic film. If we imagine, instead of the liquid film one of indiarubber, it is obvious that a given weight can only stretch this to a definite extent. To enlarge the film further additional weight would be required or, in other words, the stress per unit length is not independent of the size of the surface, but increases with the extension of the latter.

We now return to a consideration of what occurs when we stretch the liquid film in the arrangement referred to above. For the sake of simplicity, we assume the width CD to be unit length, and we shift the wire CD, with the weight equal to surface tension per unit length, again through unit length. Remembering that the work done is measured by (applied force × distance through which it moves the body acted upon) we see that the work done is equal to (surface tension × unity) and this goes to increase the energy of the surface. Thus, *the work*

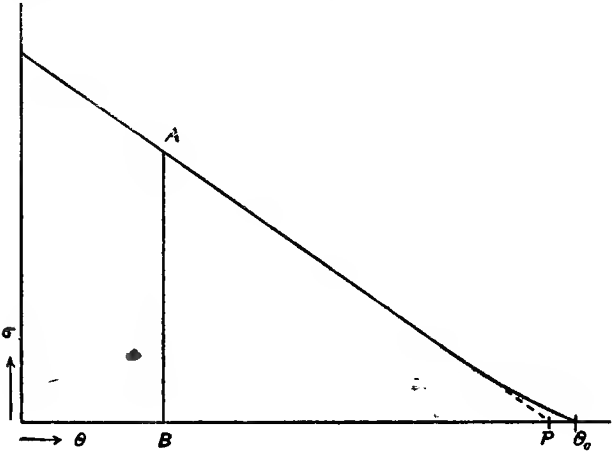

FIG. 2.

done when the surface is increased by unity is numerically equal to the surface tension, the temperature being constant. Consistent units must of course be used ; if the surface tension is given in dyne/cm., the work is given in ergs. (An erg is the work done when one dyne moves the point to which it is applied through a distance of 1 cm.)

The following values of the surface tension of various liquids (all in dyne/cm.) will help to give some idea of the order of forces we are dealing with :

Water	at 18°	73
Mercury	,, 15°	436
Glycerine	,, 18°	65
Aniline	,, 20°	43·8
Chloroform	,, ,,	26
Ethyl alcohol	,, ,,	22
Ethyl ether	,, ,,	16·5

We shall, in the following, use the symbol σ to designate surface tensions generally.

The mention of the temperatures in connection with the figures given above suggests that the value of surface tension varies with the temperature, and this is indeed the case. If we call

θ the temperature
σ_θ the surface tension at that temperature
σ_0 the surface tension at 0°

σ_θ is given by the following equation :—

$$\sigma_\theta = \sigma_0 (1 - a\theta),$$

in which a is a constant, *i.e.,* the surface tension decreases as the temperature rises ; it becomes zero at the critical temperature of the liquid. The equation, which holds good for temperatures more than about 40° below the critical temperature, is that of a straight line. If we plot θ as abscissæ and σ as ordinates, the straight line intersects the θ axis at a point P about 6° below θ_c. (Fig. 2). The surface tension AB at any temperature θ is then proportional to PB, or $\sigma_\theta = b.\,\mathrm{BP}$, where b is a constant depending on the nature of the liquid. If the temperature corresponding to the ordinate AB is θ, we have

$$\mathrm{B}\theta_c = \theta_c - \theta \text{ and } \mathrm{PB} = \theta_c - \theta - 6,$$

and obtain the following general expression for the surface tension at any temperature

$$\sigma_\theta = b\ (\theta_c - \theta - 6).$$

This knowledge of the law connecting surface tension and temperature enables us at once to decide a highly important question, viz., whether the production of surface energy is accompanied by any temperature changes, in other words, by the liberation or absorption of heat. We can solve this question by applying the principle of Le Chatelier, which says that, when the state of a system is changed, the system alters so as to oppose a greater resistance to that change. A few instances will make the principle and its application clear. If air is suddenly compressed, it becomes hotter, and thereby tends to expand, *i.e.*, to resist the compression. If current is passed across a junction of two metals, a back electromotive force is set up, tending to produce a current flowing in the opposite direction. Dissolving a salt in water causes cooling, this being a change which opposes a greater resistance to further solution, as the solubility decreases with falling temperature. By similar reasoning, we find at once that a liquid film is cooled when suddenly stretched, because its surface tension is thereby increased, and it opposes a greater resistance to further extension. Hence it follows that, if a surface is increased isothermally (*i.e.*, without a change in temperature), heat must flow into the surface film to keep its temperature constant. The amount of heat required to do this was first calculated by Lord Kelvin.

We now consider once more, in the light of the foregoing, the enlarging of the surface in the arrangement shown in Fig. 1. If CD is pulled outwards a distance x, the work done on one side of the film is

$$w = \sigma \, . \, \mathrm{CD} \, . \, x$$

or, if we call CD . x, the increment in surface, ds, the work is

$$w = \sigma \, . \, ds$$

σ, as already explained, is numerically equal to w' (consistent units being assumed), the amount of work required to produce an increase in surface of 1 sq. cm., the temperature remaining constant. This work, of course, goes to increase the surface energy, but *it is not correct to define the surface tension as surface energy/cm²*, since there is in addition an inflow of heat, which also increases the energy. Thus, with water at 0°, σ is 75 dyne/cm., and the work required to produce 1 sq. cm. of surface is 75 ergs; in addition to this there is an inflow of heat which, reduced to units of work, amounts to about 40 ergs.

The *total energy* of the surface, therefore, consists of two terms, of which one represents the amount of work done against surface tension, and the other the inflow of heat during the extension of the surface. If we call this total energy λ, the following equation, given by Kelvin, expresses the connection between surface tension and total energy at any temperature :—

$$\sigma = \lambda + \theta \frac{d\sigma}{d\theta}$$

$\frac{d\sigma}{d\theta}$ is the differential coefficient of the function which expresses the variation of surface tension with temperature. We know already that this is a linear function over a considerable range, and that surface tension decreases with increasing temperature, so that the differential coefficient becomes a constant and negative, viz., $\frac{d\sigma}{d\theta} = -c$. Over the same range λ, the total energy, is a constant.

We are naturally interested in connecting a physical constant, like surface tension, with other physical constants, and one such connection is immediately suggested by the decrease in surface tension caused by an increase in temperature. It is only natural to inquire whether there is any parallelism between this and the most obvious change produced in a liquid by increasing temperature: expansion. Measurements have shown that this is indeed the case, and that there is marked parallelism between the temperature coefficient of surface tension, *i.e.*, the decrease caused by a rise in temperature of one degree, represented by the constant a in our first equation, and the coefficient of expansion. The greater the latter, the greater also is the decrease in surface tension per degree, and the ratio temperature coefficient/coefficient of expansion is approximately the same—between 2 and 3—for a very large number of liquids. Some explanation of this fact, as well as many other connections between surface tension and various physical constants will be suggested by theoretical considerations, to which we now proceed.

The theory of surface tension, in other words, the problem how certain known facts and certain assumptions about the liquid state can be made to account for the existence of a surface tension, has been treated exhaustively by Laplace, by Gauss, and more recently by Van der Waals. The mathematical apparatus employed is very considerable, and we must confine ourselves to a statement of the assumptions on which the simplest of the theories, that of Laplace, is based.

Laplace assumes that the molecules of a liquid attract one another with forces acting over very small distances only. The distance beyond which this attraction becomes imperceptible is known as the radius of molecular action, and various considerations, into which we cannot go, lead to a value of about 5×10^{-7} cm., or 5 $\mu\mu$ for this radius. It is obvious that forces of this kind, which are inappreciable at distances of, say, 1 mm., may yet be enormous in the small space in which they are operative. Such a conception is naturally somewhat difficult, but becomes easier if we consider a parallel case, that of adhesion between surfaces in contact. This is also caused by attraction, effective only over such short distances that the slight irregularities of even smooth surfaces prevent it from acting. Yet copper, for instance, can be polished to such a degree that a cube of the metal will support eleven others merely by adhesion. This means that 1 sq. cm. of surface carries a copper prism 1 cm. square and 11 cm. long, which accordingly weighs 98 gms. Yet a slightly insufficient polish or the presence of some particles of polishing material renders this attractive force inoperative.

Granting Laplace's fundamental assumption, we see that the molecules in the interior of a liquid are subject to attraction in all directions, but that a different condition prevails in a layer at the surface, the thickness of which is smaller than the radius of molecular action. In this layer the molecules are subject to unbalanced attraction from the adjoining molecules in the interior, in other words, to an inward pull, which keeps the surface in a state of tension. If we imagine a small prominence raised somewhere in the surface, the tendency of this inward pull would be to bring it into the general level of the surface, and the effect is the same as that of an elastic membrane covering the surface, to return to the simile employed at the beginning.

A further conclusion, however, remains to be drawn which is less familiar. The effect of the mutual attraction between molecules must be the same as that of a pressure existing in the liquid, and this is called the *intrinsic pressure.* A liquid must, therefore, oppose a resistance to forces tending to enlarge its volume or, in other words, must possess cohesion or tensile strength. We habitually overlook this fact, only because we handle liquids almost exclusively under conditions which change their shape, but do not alter their volume. If, however, we attempt to do the latter, the existence of cohesion or intrinsic pressure is easily demonstrated, and some experiments in this sense will be referred to below.

It is fairly clear that the foregoing reasoning applies, not only to liquids, but also to solids or even gases, both of which ought accordingly to possess surface tension and intrinsic pressure. As regards solids, we find support for this proposition in the continuity of phenomena, which is the basis of physical science. We know that the surface tension of a liquid increases with falling temperature, and it is therefore improbable that it should suddenly disappear when the temperature falls to the freezing point and the liquid changes into solid. With gases, the case is not quite so clear, but we can say at once that, in view of the smallness of the radius of molecular action, the attraction between gas molecules must be very slight, owing to the distance between them. Thus, 1 cc. of water becomes nearly 1,700 cc. of steam at 100°, and the distance between the molecules in the latter must therefore be $\sqrt[3]{1{,}700}$, or about twelve times greater than that between the molecules in water.

Nevertheless, this molecular attraction exists and shows itself, when the gas is strongly compressed —and the distance between the molecules is greatly reduced—by causing deviations from Boyle's law. If we consider two layers of molecules, the distance between which is, of course, smaller than the radius of molecular attraction (Fig. 3), we see that their mutual attraction, or, in other words, the intrinsic pressure is proportional to the number of attracting molecules and to the number of attracted molecules, that is, proportional to the square of the number of molecules. The number of molecules in unit volume is obviously proportional to the density, and we can, therefore, say that the intrinsic pressure is proportional to the square of the density

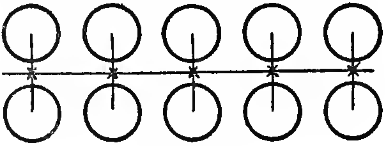

FIG. 3.

$$P = a\rho^2$$

where a is a constant and ρ the density. If we now call v the specific volume, *i.e.*, the volume occupied by 1 gm., $v = 1/\rho$, and we can write

$$P = \frac{a}{v^2}$$

This term enters into Van der Waals's equation for the volume of a gas at the pressure p and the temperature θ

$$\left(p + \frac{a}{v^2}\right)(v - b) = R\theta$$

and its value can be determined from the observed deviations of a gas from Boyle's law. If we assume that Van der Waals's equation applies approximately to liquids, as it undoubtedly does near the critical temperature, we find the intrinsic pressure of water to be about 11,000 atmospheres.

In view of the surprising value obtained in this way, it is desirable that we should have an alternative method of evaluating the intrinsic pressure. Such a method is available and is more instructive for our purpose, as it connects the intrinsic pressure with another important physical constant, the latent heat of vaporisation. This is the amount of heat required to transform 1 gm. of liquid into vapour without changing its temperature; for water at 100°, for instance, the latent heat $L = 540$ calories. To establish a connection between this constant and the intrinsic pressure we have to consider the work done in vaporising a liquid. This is of two kinds: molecules must be brought from the interior to the surface of the liquid and carried into the space above, against the pull exerted by the rest of the liquid, and the vapour thus produced must lift the superincumbent atmosphere. The portion of the latent heat used in doing the first part of the work is called the internal latent heat, L_i, since it arises from internal cohesive forces, while the portion used to overcome atmospheric pressure is called the external latent heat, L_e, which depends on the volume of the vapour and the atmospheric pressure to be overcome. If we call the atmospheric pressure, expressed in dynes, p, and the volume in cubic centimetres of 1 gm. of vapour v, the external latent heat $L_e = pv$ ergs, or pv/J calories, where J is the mechanical equivalent of heat, 42×10^6. For water at 100° L, as mentioned, is about 540 calories, L_e about 40 calories, and L_i accordingly about 500 calories, or, in units of work, $500 \times 42 \times 10^6 = 21 \times 10^9$ ergs.

To connect the internal latent heat with the intrinsic pressure let us consider the forces to which a molecule of the liquid is subject. As long as it is in the interior of the liquid these are obviously equal in all directions, but the case is different when the molecule approaches the surface nearer than the radius of molecular attraction. Let O (Fig. 4) be such a molecule and describe round it a sphere with the radius C of molecular attraction; then only the liquid within that sphere will have any effect on O. In the position shown the molecule is attracted downwards by the liquid contained in the segment *ab* (equal to AB), as the downward attraction of the slab *abcd* is balanced by the upward pull of the slab AB*cd*. This downward pull evidently increases until O is in the surface and decreases as O rises further above the surface, to become zero when the distance of O from the surface becomes C. It is, therefore, obvious that half the work of moving the molecule from the interior of the liquid into the space above is done when the molecule is brought into the surface, and that the other half is used in dragging the molecule off the surface. The total work is, as explained above, the internal latent heat L_i, if we consider 1 gm. of liquid, and the work done in taking this gramme off the surface is therefore $\frac{1}{2} L_i$. It can be shown that this work is also equal to P ergs, where P is the intrinsic pressure

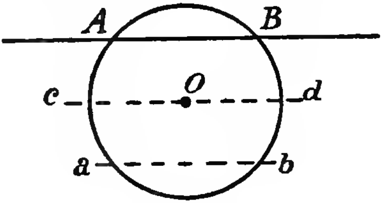

FIG. 4.

expressed in dynes. We thus obtain the following value for P:—

$$P = \tfrac{1}{2} \times 21 \times 10^9 \text{ dynes},$$

or, since an atmosphere is approximately 10^6 dynes,

$$P = \tfrac{1}{2}. \times 21 \times 10^3 = 10{,}500 \text{ atmospheres}.$$

This value is in good agreement with the one obtained from Van der Waals's equation.

The magnitude of this cohesive force is surprising, and it is desirable to have experimental demonstration of its existence and value. Experiments for this purpose have been made by various investigators, one of the first being due to Berthelot. He filled a narrow tube almost completely with water, a small bubble of vapour only being left in it. The tube was then warmed till the bubble disappeared and the water filled the whole tube. The tube could then be cooled without the bubble reappearing at once, so that the liquid was evidently stretched, the increase in volume in Berthelot's experiment amounting to about 1/400 of the total. The stress produced in the liquid by this extension could, of course, not be measured in the arrangement just described. This was, however, done by Worthington, who introduced into the tube a small bulb, with a capillary stem, filled with mercury. When the external liquid was stretched, as in Berthelot's experiment, the bulb expanded and the mercury indicated the amount of stress. Worthington examined the behaviour of alcohol between + 12 and — 17 atmospheres pressure, and obtained the very important result that the modulus of elasticity was the same for extension and compression between these limits. In other words, the force required to increase the volume of a given body of liquid by a certain amount is the same as that required to decrease it by the same amount, *i.e.*, to compress it. This means that the greater the pressure required to compress a given liquid, or, in other words, the smaller its compressibility, the greater will its intrinsic pressure be. The compressibility of many liquids has been determined and is generally given as the coefficient of compressibility, *i.e.*, the reduction of unit volume by one atmosphere pressure. It is 48×10^{-6} for water, 105×10^{-6} for ethyl alcohol and 190×10^{-6} for ether. The intrinsic pressures for these liquids, calculated from Van der Waals's equation, are respectively about 11,000, 2,400 and 1,400 atmospheres, and show strikingly how the intrinsic pressure decreases as the compressibility increases.

The relations between the intrinsic pressure and other physical constants developed in the foregoing paragraphs have been found from theoretical considerations based on Laplace's theory, that is, on the assumption of cohesive forces acting over very small distances. They are of interest to us inasmuch as there is a necessary connection between intrinsic pressure and surface tension. While no numerical expression has so far been found for this, it is obvious that high intrinsic pressures must be accompanied by high surface tensions, since the surface tension is a manifestation of the same cohesive force as causes intrinsic pressure. (See, however, equation 3, p. 27, for an empirical relation between the two.)

CHAPTER II.

We now proceed to the consideration of a number of relations between surface tension and other physical constants which have been established largely by experiment. In view of what has been said at the conclusion of the preceding chapter, it is obviously of interest to examine the relation between surface tension and compressibility in a number of cases. We have found that a high intrinsic pressure means a low compressibility, and *vice versâ*, and have concluded that surface tension goes parallel with intrinsic pressure. High surface tensions should accordingly be accompanied by low compressibilities, and this reasoning is borne out by the following table, in which the surface tensions σ are given in dynes/cm., while the compressibility coefficients β are all multiplied by 10^6.

TABLE I.

Liquid.	σ	β
Mercury . . .	440	3·83
Water	75	48
Benzene . . .	28	92
Ethyl alcohol . .	21·6	105
Ethyl ether . . .	16	190
Acetic acid . . .	23	88
Glycerine . . .	65	52

While the general trend of the figures is as we predicted, we find that, for instance, acetic acid and glycerine exhibit considerable anomalies. These are liquids known from other evidence to be highly associated; if we exclude such associated liquids the agreement is improved, although even then the product $\sigma \cdot \beta$ is not a constant. Richards and Matthews have found that for a fair number of

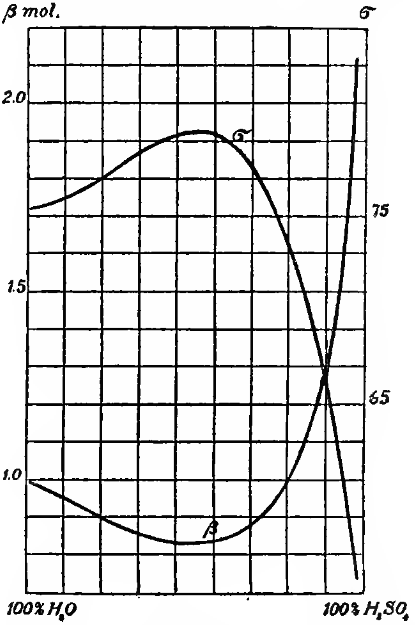

FIG. 5.

liquids (covering, however, only a small range of σ) the product $\sigma \cdot \beta^{\frac{4}{3}}$ is a constant.

It is only reasonable to suggest that the compressibility of a liquid may depend partly on the shape of the molecules, and that we should, therefore, expect only a rough relation between σ and β, as we go from one liquid to another. We can eliminate this factor by keeping to the same molecules, for instance, by working with solutions of the same substance but of different concentrations. In this case the product $\sigma \cdot \beta$ is more nearly constant, but still better agreement is obtained if, instead of taking the reduction of unit volume as β, we take the change in volume for an equal number of molecules, which we may call the molar compressibility. This has been done by Röntgen and Schneider for mixtures of sulphuric acid and water, and the curves obtained for σ and the molar β are shown in Fig. 5.

The connection between surface tension and the coefficient of thermal expansion has already been referred to in Chapter I. We have next to consider the relations between surface tension and vapour pressure, which are of considerable importance in a number of physical processes.

A bubble of air in a liquid is, as we know, spherical, and it is obvious that this spherical shape can only be maintained if the pressure on the inside is greater than that outside. Let P be the excess of pressure inside per unit surface, and a the radius of the sphere: the pressure tending to force the two hemispheres apart is then evidently P × area of largest circle, *i.e.*, $P \cdot \pi a^2$. This pressure is balanced by the pull arising from surface tension, which acts round the circumference of the same circle, and is, accordingly, $2\pi a\sigma$. We have, therefore,

$$P \, . \, \pi a^2 = 2\pi a\sigma \text{ or } P = \frac{2\sigma}{a}.$$

(If we consider, not a bubble submerged in liquid, but one surrounded by a thin film of the same, *e.g.*, a soap bubble, we have to take into account the pull on both the internal and external surfaces, so that the pressure excess $P = \frac{4\sigma}{a}$.)

The excess pressure, being inversely proportional to the radius, becomes very considerable for small bubbles. As it balances the surface tension, a further rise in pressure is necessary if the bubble is to expand. If, therefore, only small bubbles of vapour are formed in a liquid, the temperature must be raised considerably above the boiling point before the bubbles expand and boiling occurs; when this happens, it does so suddenly and with violence, or, as it is usually termed, the liquid boils "by bumping." It is well known that this can be prevented by introducing into the liquid some porous body containing air, so that the formation of large bubbles is ensured.

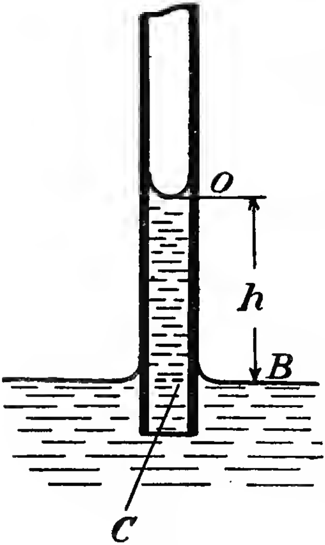

Fig. 6

We have established a connection between the pressure on a liquid surface and its curvature by the formula given above. No assumption is made as to the cause of the pressure, and it remains to be seen whether we can introduce the vapour pressure into the reasoning, and thus connect this constant with the surface tension.

Such a relation between surface tension and vapour pressure was first established by Lord Kelvin, who demonstrated that the vapour pressure over a curved surface must be different from that over a plane surface of the same liquid. His proof cannot be given here, but the following simple considerations clearly show the connection between curvature of surface and vapour pressure, and lead to an approximate formula expressing the latter in terms of surface tension and radius of curvature.

Consider a capillary immersed in water (Fig. 6) in which the liquid has risen to a higher level than that outside. As we ascend in the vapour from the plane surface, the vapour pressure decreases—exactly as the atmospheric pressure decreases when we rise from a lower to a higher level. If we call the vapour pressure at the level of the plane surface p, and that at the height h above it p', the latter is less than the former by an amount

$$p - p' = h\rho' g$$

where ρ' is the vapour density, which we assume to be constant over this small height, and g the gravity constant. Hence the vapour pressure in equilibrium with the concave liquid surface in the capillary is smaller than that on the plane surface. To obtain the difference we proceed as follows: The pressure at a point C in the capillary, which is on the level of the plane surface, B, must be equal to that on the latter, else there would be a flow of liquid in one direction or the other. If we imagine the whole arrangement placed in a vacuum, the pressure on B is simply the vapour pressure p. The pressure just above the curved surface at O, which we assume to be hemispherical, is greater than that just below it, and we have shown above for an air bubble in liquid that this difference of pressure is $\frac{2\sigma}{a}$, where a is the radius of the surface. The pressure above the surface is of course p', and the pressure just below the surface is accordingly $p' - \frac{2\sigma}{a}$. The pressure at the level C is then obviously equal to this pressure *plus* the weight of the column h of liquid, *i.e.*, if we call the density of the liquid ρ

$$\text{Pressure at C} = p' - \frac{2\sigma}{a} + h\rho g.$$

As explained above, the pressure at C is equal to that at B, which is the vapour pressure on a plane surface, p, and we have accordingly

$$p = p' - \frac{2\sigma}{a} + h\rho g \text{ or } p - p' = h\rho g - \frac{2\sigma}{a}.$$

We know from above that $p - p' = h\rho' g$, and by introducing this value we obtain

$$h\rho' g = h\rho g - \frac{2\sigma}{a} \text{ or } \frac{2\sigma}{a} = hg(\rho' - \rho) = hg\rho' . \frac{\rho' - \rho}{\rho'}.$$

If we finally reintroduce the value $p - p'$ for $hg\rho'$, we arrive at the equation

$$\frac{2\sigma}{a} \frac{\rho'}{\rho' - \rho} = p - p'$$

which establishes the desired relation between surface tension and radius of curvature on one hand, and the difference between the vapour pressures on the plane and curved surface on the other hand.

(This formula is only approximate ; a stricter calculation leads to the equation

$$R\theta \log_e \frac{p}{p'} = \frac{2\sigma}{a\rho}$$

where R is the gas constant and θ the absolute temperature.)

In arriving at our formula we have assumed that the liquid in the tube stands at a higher level than outside, and that its surface is concave, which is the case when the liquid wets the tube, as for water or alcohol. If the liquid does not wet the tube, *e.g.*, mercury—the level in the capillary is lower than that outside and the surface is convex. Our reasoning, however, still applies, and leads to the conclusion that the vapour pressure on the convex surface is greater than that on the plane surface. The formula covers both cases, since the radius must be given the opposite sign if the curvature is in the opposite direction; it is positive when the surface is concave.

The approximate formula shows immediately that the smaller is a, the radius of curvature, the greater is the difference between the vapour pressure at the curved and at the plane surfaces. For very small values of a the difference becomes very marked; if we have a spherical drop of water at 0° with a radius ·001 mm. or 1 μ, the equilibrium vapour pressure is greater than that at a plane surface by one part in a thousand, but if a is only 10^{-6} mm. or 1 $\mu\mu$, the equilibrium pressure required is more than double that at the plane surface. If the vapour in which such drops are suspended has the pressure corresponding to a plane surface, the drops will therefore tend to evaporate very rapidly; similarly, if drops of different sizes are present together, the large ones will grow at the expense of the small ones. The high vapour pressure of very minute drops also makes it difficult for condensation to begin in dust-free air; if dust particles are present and act as nuclei, the drops start their life with a fairly large radius, so that the equilibrium vapour pressure and, consequently, the tendency to evaporation are reduced. Air entirely free from dust may be cooled to a temperature so low that the moisture present is eight times that required to saturate it before any fog is formed.

Similar considerations apply to the behaviour of porous bodies in an atmosphere containing vapour. Pores are substantially collections of capillary tubes. If the liquid whose vapour is present wets the body, the resulting surface is concave and the equilibrium pressure is therefore lowered, so that it is easy for condensation to take place in pores, even if the atmosphere is not saturated with vapour. This may account in part for the absorption of water by cotton wool, flannel, etc., although some of it is no doubt due to adsorption, which will be treated later.

We shall now proceed to show that a reasoning analogous to that which led us to conclude that large drops of liquid grew at the expense of small ones can be applied to establish a very interesting relation between surface tension and the solubility of solids. Before doing so it is advisable to amplify what has been said already about this somewhat difficult subject, the surface tension of solids. We have already concluded that the surface energy of a liquid, which increases steadily with falling temperature, cannot disappear suddenly when the freezing point is reached, *i.e.*, when the liquid changes into a solid, so that the latter must necessarily possess surface energy and surface tension. The reasoning is further strengthened by the well-known fact that many amorphous substances, at least, behave in other respects like liquids of extremely high viscosity. Thus steel balls placed on pitch gradually sink through it ; asphalt and marine glue spread over glass plates at ordinary temperatures and pressures unless confined ; a stick of sealing wax clamped at one end in a horizontal position gradually sags, etc., although all these substances are at the same time sufficiently solid to give out a note when touched with a vibrating tuning fork. Since they all possess surface tension when liquid, we are forced to conclude that they also do so when solid, and that the surface tension then has a very high value. In the case of crystalline solids the analogy to liquids is much less complete, but still there is nothing to warrant us in supposing that the surface forces disappear at freezing; all we know is that their action is profoundly modified, and is presumably different in different directions or on different faces of the crystals.

To return to our problem, we may regard the growth of big liquid drops at the expense of small ones as resulting from the transfer of a quantity of liquid *m* from one to the other. Since the big drop has a smaller surface than an equal volume of small ones, this transfer leads to a decrease of surface energy and at the same time liquid is taken from a place of higher to a place of lower vapour pressure. The growth of particles in a precipitate or in a supersaturated solution is found to occur in a similar manner, *i.e.*, large crystals grow at the expense of small ones; but here we have to deal with the decrease in energy of a surface solid-liquid (instead of liquid-vapour) and the transfer of matter from a place where the osmotic pressure (instead of the vapour pressure) is higher to one where it is lower. The calculation was first carried out by Wilhelm Ostwald, subsequently corrected by Hulett, and leads to an equation formally identical with that given above

$$R\theta \log_e \frac{p'}{p} = \frac{2\sigma}{\rho a}$$

in which however, p is now the osmotic pressure in equilibrium with a large surface, *i.e.*, the ordinary osmotic pressure, p' that in equilibrium with a surface of the radius $-a$, σ the surface tension solid-liquid, and ρ the density of the solid.

The osmotic pressures are proportional to the number of molecules dissolved in the same volume, or, in other words, to the solubilities of large and small particles respectively, and will be different if these solubilities are different. The latter is actually the case for the two substances examined by Hulett, calcium sulphate and barium sulphate.

The solubility of the former (determined by electrical conductivity measurements) was 18·2 millimoles per litre for particles of a radius $a = {\cdot}00003$ cm., and 15·33 millimoles for particles of a radius $a = {\cdot}0002$ cm., so that the smaller particles show a considerably larger solubility. Since the osmotic pressures are proportional to the amounts dissolved, we can write

$$\frac{p'}{p} = \frac{\lambda'}{\lambda}$$

where λ and λ' are the respective solubilities, and the formula thus becomes

$$R\theta \log_e \frac{\lambda'}{\lambda} = \frac{2\sigma}{\rho a}$$

It can now be used for the extremely important purpose of calculating σ, which is found to be 1,100 dyne/cm. for calcium sulphate and 4,000 dyne/cm. for barium sulphate. These figures entirely confirm the conclusion to which we have come on general grounds, that the surface tensions of solids must have high values. The applicability of the Ostwald-Hulett formula is limited, since it is based on Van 't Hoff's equation for osmotic pressure, which only holds for small concentrations and, therefore, in the present case, for low solubilities.

The growth of large crystals at the expense of small ones occurs, not only in solutions, but also under conditions which resemble even more closely the growth of large drops, *i.e.*, by sublimation. The phenomenon has been observed in the case of sulphur and of sulphur trioxide in an evacuated space, and in the case of camphor crystals condensed from the vapour on a cold glass surface.

CHAPTER III.

We have so far succeeded in establishing connections between surface tension and a number of physical properties, but have not yet found a relation between the former and any chemical constant. A very simple and general relation of this kind was first pointed out by the Hungarian physicist Eötvös and confirmed experimentally, for a large number of liquids, by Ramsay and Shields. If M is the molecular weight of a liquid and ρ its density, then $\left(\frac{M}{\rho}\right)$ is proportional to the volume of a molecule. $\left(\frac{M}{\rho}\right)^{\frac{1}{3}}$ is then proportional to the linear dimension of the molecule, and $\left(\frac{M}{\rho}\right)^{\frac{2}{3}}$ to its surface area. Also, if σ, the surface energy per square centimetre of a molecule, is assumed to be the same as that of the liquid in bulk, the product $\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}$ represents the molecular surface energy. The Eötvös-Ramsay-Shields formula states that

$$\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}} = K(\theta - \delta)$$

where θ is the amount by which the temperature at which σ is measured lies below the critical temperature.

The important point is that for $\delta = 6°$, the value of K is the same—approximately 2·1—for a very large number of different liquids, independently of their nature.

In the case of some liquids—*e.g.*, water, acetic acid and others—however, divergent values of K are obtained. Thus if we apply the formula to water at 0°, when $\sigma = 75$, $\rho = 1$ and $\theta = 365$, and if we put $M = 18$, we obtain a value of K much smaller than 2·1. But σ has also been determined between 100° and 200°; if we introduce the values found in that range for σ and ρ *and put* $M = 36$, then K becomes approximately 2·1. This is interpreted to mean that at the temperatures selected water has the molecular weight 36, or that it consists of aggregates containing two molecules on the average. Similarly, if K is to have its normal value below 100°, M must have a value between 36 and 54, *i.e.*, water at these temperatures must consist of aggregates some of which contain two and some three molecules. Whenever K has an abnormally low value the liquid is thus assumed to be associated. Of course this is not the only possible explanation of the results, and there should be some confirmatory evidence of association, which must show itself in other anomalies, for instance, of density and thermal expansion (water), or of density of solutions (acetic acid in water). Failing such evidence, other interpretations are possible; it might be that water is non-associated, but that its molecular surface energy is smaller than that assumed. On the modern view of the atom as a dynamical system it is also difficult to form any ideas as to where the molecular surface energy has its seat.

The Eötvös-Ramsay-Shields formula represents the most important relation between surface tension and molecular weight so far established. A number of other and very interesting connections have, however, been pointed out by Walden in a series of papers published in 1908 and 1909, to which we can refer only briefly. In his equations the surface tension does not appear directly, but a constant derived from it—the introduction of which, although fairly general with German authors and although the constant has a definite meaning in Laplace's theory, has very little to recommend it. This constant is called the *specific cohesion* and is defined as $a^2 = \frac{2\sigma}{\rho}$ where σ and ρ have the usual meanings. Its dimensions are those of a surface, L^2.

The principal relations established by Walden are as follows:—

$$(1) \qquad \frac{L_b}{a_b^2} = 17{\cdot}9$$

where L_b is the latent heat of vaporisation in calories, and a_b^2 is the specific cohesion (as defined above) at the boiling point. This formula holds good for normal, *i.e.*, non-associated liquids; associated liquids give higher values.

$$(2) \qquad \frac{ML_b}{v\sigma_b} = 3{\cdot}64$$

where L_b has the same meaning as above; M is the molecular weight, v the molecular volume, and σ_b is the surface tension at the boiling point. This relation again holds only for non-associated liquids.

$$(3) \qquad P = 75{\cdot}3\,\sigma_b$$

where σ_b has the same meaning as before and P is the intrinsic pressure in atmospheres. This relation is interesting on account of its great simplicity, but has little practical value, owing to the impossibility of directly determining the intrinsic pressure.

(4) By comparing the intrinsic pressures of various liquids and their solubilities in water, Walden finds that there is parallelism between the two. He

also finds generally, although without establishing any numerical relations, that the mutual solubility of two liquids is the greater the smaller the difference of their intrinsic pressures ; if this difference is very great the liquids are practically immiscible.

Two further relations introduce the melting point and the latent heat of fusion. They are :—

$$(5) \qquad \frac{L_m}{a_m^2} = 3{\cdot}6 \text{ (approximately)}$$

where L_m is the latent heat of fusion and a_m^2 the specific cohesion at the melting point.

$$(6) \qquad \frac{Ma_m^2}{\theta_m} = 3{\cdot}65$$

where M is the molecular weight, θ_m the absolute temperature at the melting point, and a_m^2 has the same meaning as before. This relation holds good only for non-associated liquids, and can, therefore, like the Eötvös-Ramsay-Shields formula, be used for determining the "association factor" of associated liquids. The results obtained by using the latter do not, however, agree in all cases with those following from Walden's formula ; thus, benzene is associated according to Walden and non-associated according to Ramsay. The discrepancy is particularly striking in the case of sulphuric acid, which has aggregates consisting of as many as thirty-two molecules according to Ramsay, while Walden finds aggregates of two molecules only.

In connection with the melting point an interesting fact deserves mention, viz., that this temperature varies with the size of the particles. This is a striking parallel to the variation of solubility with size discovered by Ostwald and Hulett, and referred to in Chapter IV. Thus, Pawlow finds that granules of salol with a surface of 230—1,300 μ^2 have a melting point 2·9° lower than particles with a surface 100 times greater, *i.e.*, with ten times greater diameter.

In the preceding pages a large number of relations between surface tension or intrinsic pressure and other physical and chemical constants have been given—some theoretical and some empirical. We have now to deal briefly with an attempt to connect surface tension with another property of solutions—their osmotic pressure—not so much because this attempt can be called at all successful, but because it has received a good deal of attention, especially in biological work. The reader must be assumed to possess a general knowledge of the theory of osmotic pressure, but, as we shall have to refer to the subject again in connection with the important phenomenon of adsorption, a few remarks on this theory may be useful.

If a solution and the pure solvent are separated by a semipermeable membrane, the solvent tends to pass through the membrane into the solution, and the osmotic pressure is the pressure that must be applied to the latter to keep the solvent from entering into it. The term " osmotic pressure of the solution " is, therefore, strictly speaking, incorrect, as osmotic pressure is, according to the definition, produced only when the solution is separated from the solvent by a semipermeable membrane. If this is remembered, it disposes of the objection sometimes raised that osmotic pressure " works the wrong way," in that it causes motion from places of lower to places of higher osmotic pressure. It is osmosis which causes osmotic pressure, and not osmotic pressure which produces osmosis.

The simple theory of osmotic pressure developed by Van't Hoff is well known. According to it the molecules of solute behave like gas molecules, and produce the same pressure as would be produced by an equal number of gas molecules occupying the same volume at the same temperature. This leads to a formula for the osmotic pressure which is formally identical with that connecting pressure, temperature and volume of a gas, viz. :—

$$p = R\theta c$$

where p is the osmotic pressure, θ the absolute temperature, c the concentration, expressed in grammes per cubic centimetre, or more usually in gramme-molecules per litre, and R a constant depending on the units in which the concentration and pressure are expressed.

From the assumptions made in deducing it, it appears that this formula is inapplicable to any but dilute solutions. At higher concentrations the discrepancies become considerable between the osmotic pressures actually measured and those calculated from Van't Hoff's equation. The following figures for cane sugar may serve as an example :—

c	p (observed)	p (calculated)
180 gm/litre	13·9 atm.	11·8 atm.
750 gm/litre.	133·7 atm.	49·4 atm.

The attempt to show that surface tension phenomena were the cause of osmotic pressure was first made by Jäger, and his theories were vigorously supported and developed by Traube, whose conclusions we shall state and examine briefly. He finds that the more a dissolved substance reduces the surface tension of water the greater is the velocity of osmosis of the solution. Hence he concludes that it is the difference in the surface tensions of solvent and solution which determines the direction and velocity of osmosis. The direction of flow Traube obtains by the following consideration: let M (Fig. 7) be a membrane separating two liquids A and B. The molecules of each liquid are then drawn into its interior by the cohesion or intrinsic pressure. If the intrinsic pressure of A is greater than that of B, the latter liquid will pass through the membrane, or will have the power to do so. Since a large intrinsic pressure means a large surface tension, this is equivalent to saying that B passes into A if the surface tension of A is higher than that of B.

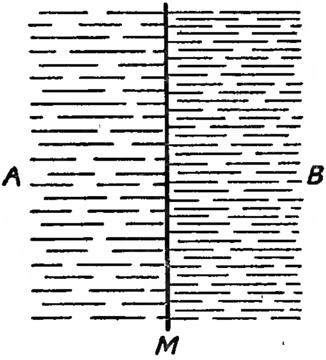

FIG. 7.

If the membrane is removed and A is a solution while B is water, then B (water) diffuses into A (solution), but not A into B.

Traube further expands these considerations by applying them to the explanation of solubility. He ascribes the process of solution to the difference in the surface tensions of the solid and liquid, and assumes that saturation is reached when the two surface tensions have become equal.

It may be remarked here that Traube's theory is rather a theory of osmosis than of osmotic pressure and that, as regards the latter, it has proved incapable of giving any numerical results. It is also open to a number of grave objections, which we will state very briefly. A solution of salicin in water has lower surface tension than water, yet water passes into it through a membrane, as it also does into a mixture of ethyl alcohol and water. According to Traube's theory this should be impossible. A further deduction from Traube's theories has also proved untenable. According to them, no diffusion through a membrane from a solution into the solvent should be possible if the former has a higher surface tension than the latter; in other words, the membrane behaves as an impermeable membrane to this system. Traube assumes that it becomes permeable, *i.e.*, that diffusion takes place, if a substance is added to the solution which reduces its surface tension below that of the solvent. This assumption has also been proved incorrect by experiment.

In view of the great importance of osmotic phenomena in organisms and of the difficulty of explaining many of them by the classical theories, Traube's views have received some attention from biologists and have given rise to various investigations, one of which deserves mention. This was carried out by Czapek, with the object of determining the "surface tension" of the contents of plant cells. He made solutions of various organic substances, in which the cells were immersed, and noted the concentrations at which the contents just began to diffuse outwards. In accordance with Traube's theories he assumed that at this point the surface tension of the solution and that of the plasma were equal. Exosmosis occurred with all solutions when their surface tension was reduced to ·65 to ·68 that of water, whence Czapek concludes that this is the surface tension of the cell contents. While we cannot consider this conclusion warranted, the fact that solutions of equal surface tension produce exosmosis is certainly remarkable. It seems probable that an explanation may be found in adsorption, as has been the case with many "poisoning" phenomena which could not be explained by osmotic pressure alone.

In the preceding pages we have availed ourselves of only one of the theories of surface tension, that of Laplace. It has led us directly to recognise an important property of liquids—their cohesion or intrinsic pressure—and has enabled us to establish several theoretical relations between surface tension and other constants. It is, however, incomplete in one particular, inasmuch as it assumes that there is a perfectly sharp line of demarcation between the two media bounding the surface, for instance, between liquid and air. We need not discuss whether such an abrupt transition is intrinsically probable, as there is a large amount of evidence, principally optical, to show that there is a gradual change in density and in other properties from those of one medium to those of the other. It can, for instance, be shown that plane polarised light should be reflected again as plane polarised light, and, therefore, be capable of being completely extinguished by a Nicol prism, if the transition from one medium to the other were abrupt. Actually this is never the case with an old surface, especially in the case of metals, but the light is always elliptically polarised. With perfectly fresh surfaces this is not the case; thus Lord Rayleigh showed that the ellipticity nearly disappeared at the boundary air-water if the surface of the latter was constantly renewed, and Drude proved its absence on the surface of a freshly split crystal.

To account for the phenomenon it is necessary to assume a film of different density on the surface, of which the order of magnitude of the thickness can be calculated, approximately; it is about 10^{-7} cm. for the surface crown glass-air. We shall have occasion to refer to this surface film again. There is also other experimental evidence for its existence; it is, for instance, a common experience in vacuum tube work that, after first pumping down and allowing the apparatus to stand, the pressure rises again owing to gas coming off the walls. Baly and Ramsay found it nearly impossible to test Boyle's law at very low pressures owing to this released gas, the amount of which varied with temperature and pressure.

The existence of such transition layers was not recognised by Laplace, but has actually been made the basis of theories of surface tension in more recent times. As these are very largely mathematical, only the briefest reference to the fundamental assumptions and the principal conclusions is possible here. The first step was taken by Gibbs, who still assumed that there is discontinuity at the boundary of two media, but that at the same time the layers of both media immediately adjoining the boundary had densities, etc., different from those of the bulk. If this assumption is granted, it can be shown that a surface tension must exist at the boundary. Gibbs developed his theory chiefly in one direction: the difference between the composition of the surface layer and that of the bulk of the medium, and we shall have occasion to refer to his work again when discussing adsorption.

Van der Waals, whose theory has been further developed by Hulshoff and by Bakker, went one step further than Gibbs by assuming that there exists a perfectly continuous transition from one medium to the other at the boundary. This assumption limits him to the consideration of one particular case; that of a liquid in contact with its own saturated vapour, and mathematical treatment becomes possible by the further assumption that the Van der Waals equation (see Chapter II.) holds good throughout the system. The conditions of equilibrium thus become dynamical, as opposed to the statical equilibrium of Laplace's theory. Van der Waals arrives at the following principal results: (1) that a surface tension exists at the boundary liquid-saturated vapour and that it is of the same order of magnitude as that found by Laplace's theory; (2) that the surface tension decreases with rising temperature and disappears at the critical point; and (3) that the thickness of the transition layer increases with rising temperature and becomes infinitely large at the critical point—which is obvious when we remember that at the critical temperature there is no difference between liquid and saturated vapour.

Van der Waals further finds a relation between the temperature coefficient of surface tension and the molecular surface energy which is in substantial agreement with the Eötvös-Ramsay-Shields formula (see Chapter V.). He also arrives at a value for the thickness of the transition layer which is of the order of magnitude of the molecular radius, as deduced from the kinetic theory, and accounts qualitatively for the optical effects described on p. 33. Finally, it should be mentioned that Van der Waals' theory leads directly to the conclusion that the existence of a transition layer at the boundary of two media reduces the surface tension, *i.e.*, makes it smaller than it would be if the transition were abrupt—a result obtained independently by Lord Rayleigh.

CHAPTER IV.

We have seen in the preceding chapters that a considerable amount of both experimental and theoretical evidence points to the existence of a transition layer at the boundary of two phases—in other words, of a layer in which the concentration of the phases is different from that in the bulk. It will, therefore, be advisable to consider quite generally what factors affect the concentration — for instance, the distribution of a solute in a solvent.

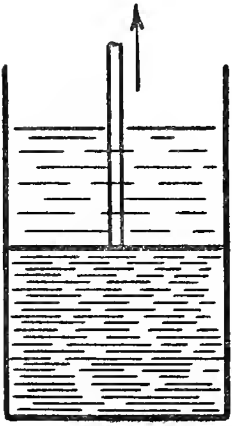

Fig. 8.

Let us assume a solution of a non-electrolyte in water, separated from the pure solvent—water—by a semipermeable membrane forming a piston (Fig. 8). Water enters the solution through the membrane and raises the piston, *i.e.*, the solution can do work or possesses potential energy owing to its osmotic pressure. If the membrane is removed, the osmotic pressure causes diffusion until (if no other forces are active) the solute is uniformly distributed through the solvent. Osmotic pressure is, therefore, a factor tending to bring about uniform concentration.

If the particles of the solute are electrically charged, work is required to bring them more closely together. This is the reason why a suspension, the particles of which are electrically charged, does not settle if the particles are sufficiently small, *i.e.*, if their weight is small compared with the forces arising from the charges on them. An electric charge on the particles of the solute is, therefore, a further factor tending to keep the particles uniformly distributed in the solvent.

A third factor governing the final distribution of the solute is the surface energy. This becomes obvious if we consider the total energy of the system. If the dissolved substance diminishes the surface tension of the solution, an excess of concentration in the surface layer diminishes the surface energy and possibly the total energy of the system. If, on the other hand, the solute increases the surface tension, the surface energy will be reduced if the concentration in the surface layer is lower than that of the bulk of the solution. This difference in concentration between the surface layer and the bulk of the solution is called adsorption and is, from our point of view, a purely physical, as distinguished from a chemical effect. It is called positive when the concentration in the surface layer is greater, and negative when it is smaller than that in the bulk of the liquid. Adsorption is evidently opposed by the factors tending to establish uniform concentration, *i.e.*, osmotic pressure and electric charge, and the final distribution of the solute is the resultant of the three effects. (See, however, Chapter V.)

The mathematical theory of adsorption was first developed by Willard Gibbs and later, independently, by Sir J. J. Thomson. We must confine ourselves to giving the result of their investigations. Let c be the concentration of the solute in the bulk of the solution and u the excess concentration, in grammes per square centimetre, in the surface layer; u is, of course, taken as positive if the concentration in the surface is greater, and as negative if it is smaller than c. We assume for the present that the solute is undissociated and that the particles or molecules are not electrically charged.

It can then be shown that

$$c\frac{d\sigma}{dc} = -u\frac{dp}{dc}$$

where p is the osmotic pressure. For dilute solutions the osmotic pressure is given by the formula :—

$$p = \mathrm{R}\theta c.$$

in which θ is the absolute temperature and R a constant, and dp is therefore

$$dp = \mathrm{R}\theta dc.$$

If we introduce these values in the first equation, we obtain

$$c\frac{d\sigma}{dc} = -u\mathrm{R}\theta \text{ or } u = -\frac{c}{\mathrm{R}\theta}\cdot\frac{d\sigma}{dc}$$

$\frac{d\sigma}{dc}$ is the differential coefficient of the function connecting surface tension and concentration and is therefore positive if σ and c increase together, and negative if σ decreases with increasing c—in other words, positive if the solute increases the surface tension and negative if it diminishes the latter. The whole product on the right hand of the equation will, therefore, be negative in the first case and positive in the second, *i.e.*, u, the excess in the surface layer, will be negative when the solute increases the surface tension and positive when it reduces it, so that there will be a lower concentration in the surface in the former case, and a higher concentration in the latter. This reasoning is conclusive, as R, c and θ are all necessarily positive and the sign, therefore, depends only on that of $\frac{d\sigma}{dc}$.

No assumption is made about the nature of the boundary, and the formula should apply to all combinations, such as solid-gas, solid-liquid, liquid-liquid and liquid-gas. If the solute is dissociated, the osmotic pressure is

$$p = i\mathrm{R}\theta c$$

and therefore (assuming that the constant i does not change appreciably with c)

$$u = -\frac{c}{i\mathrm{R}\theta} \cdot \frac{d\sigma}{dc}$$

As dissociation is, however, accompanied by the formation of electric charges, a further complication arises, to which we will refer later.

An important qualitative conclusion, which agrees with experience, can immediately be drawn from the theoretical considerations we have developed. A small quantity of dissolved substance may reduce the surface tension very considerably, but can only increase it slightly. Thus, sodium chloride increases the surface tension of water to a small extent; the concentration in the surface layer is accordingly smaller than in the bulk and the effect of the solute is thus counteracted. On the other hand, many organic salts, *e.g.*, the oleates, reduce the surface tension and therefore accumulate in the surface layer, so that, in extreme cases, the whole of the solute may be collected there and produce a considerable effect, although the absolute quantity may be exceedingly slight.

This state of things has actually been obtained with salicylic acid in a concentration of ·022 millimole per litre.

In most cases it is necessary to employ very large surfaces to obtain measurable effects, and this has been done in a variety of ways. Miss Benson examined an aqueous solution of amyl alcohol by producing a copious froth on it and comparing the alcohol concentration in the froth, which has a very large surface, with that in the bulk of the solution. Since amyl alcohol reduces the surface tension, the excess in the surface should be positive, *i.e.*, the alcohol concentration should be greater than in the rest of the liquid. The following figures confirm this conclusion :—

Original solution .. $c = \cdot 0375$ molar
Froth .. .. .. $c_1 = \cdot 0394$,,
Excess in surface .. $u = \cdot 0019$ mole

so that the concentration in the froth is about 5% higher than in the original solution.

Another method of obtaining a large surface and at the same time of demonstrating adsorption at the boundary liquid-liquid consists in allowing drops of, say, mercury to fall through a solution and determining the concentration after a certain number of such drops have passed through. Many solutes can be almost completely removed from solution in this way, *e.g.*, picric acid.

Experiments like Miss Benson's afford qualitative confirmation of the adsorption formula, but do not test it quantitatively. For this purpose it is obviously necessary to determine not only the various constants of the formula, but also, and chiefly, $\frac{d\sigma}{dc}$—in other words, to determine how surface tension varies with concentration. If we do so for a number of concentrations and plot a curve, we can deduce $\frac{d\sigma}{dc}$ from it, and we accomplish something further—we obtain a very delicate method of measuring the very low concentrations which have to be dealt with. To ascertain, for instance, the concentration in a solution after adsorption has taken place, we have only to measure the surface tension and can then at once find the corresponding concentration from the σ—c curve previously determined.

A quantitative test of the Gibbs-Thomson formula will accordingly involve the following measurements: we first determine the surface tension of a solution for a number of different concentrations, plot the σ—c curve and from it determine $\frac{d\sigma}{dc}$ for a given c. We then bring a solution of this concentration c into contact with an adsorbent, the surface of which we must be in a position to determine. After a time of contact sufficient to establish equilibrium the concentration is again determined, *e.g.*, by measuring the surface tension, and the difference represents the amount adsorbed by the whole surface of the adsorbent. This difference, divided by the surface, is therefore the amount adsorbed by the unit of surface, that is, the term u in the formula.

The procedure just outlined was adopted by Wm. C. McC. Lewis, the solution being one of sodium glycocholate in water and the adsorbing surface the interface paraffin-oil solution. The surface tension at different concentrations was determined by the drop method, to which brief reference must be made. If a drop of liquid forms at the end of a tube, it is supported by the surface tension acting round the circumference and at the moment when the drop is detached, some relation must exist between the weight of the drop and the surface forces. If we call a the external radius of the tube, m the weight of the drop in grammes, g the gravity constant, and σ the surface tension, it can be shown that :—

$$\sigma \pi a = mg \text{ or } \sigma = \frac{mg}{\pi a}$$

Lord Rayleigh has, however, found that this formula does not agree exactly with experimental results and that, for water, the denominator must be multiplied with 1·21, *i.e.*, a factor 3·8 substituted for π. The theory of this discrepancy is complicated and inexact. There is, however, no objection to the method for comparative or relative measurements, but in actual practice it is more convenient to determine the number of drops in a given volume, *e.g.*, from a pipette with two marks, rather than the weight of a drop. If the surface tension decreases, the drops will be smaller, as the smaller tension can only support a smaller drop, and the number of drops will be larger. Other things being equal, the surface tension will be inversely proportional to the number of drops. The method is applicable not only to the determination of surface tensions, but also to that of interfacial tensions of liquids against each other. It must, however, be borne in mind that, when one liquid forms drops in another, the actual weight of the drop is diminished by the weight of the liquid it displaces; if the ratio of the densities is, *e.g.*, 1 : 2, the effective weight of a drop of the heavier liquid is halved. It can easily be shown that the interfacial tension is

$$\sigma = \frac{mg}{\pi a}\left(\frac{\rho - \rho^1}{\rho}\right)$$

where ρ and ρ^1 are the densities of the heavier and lighter liquid respectively, and the other symbols have the same meaning as before.

Lewis, as already mentioned, used a solution of sodium glycocholate and determined the adsorption of the salt by a surface of paraffin oil. The σ which enters into the formula is, therefore, the interfacial tension solution—paraffin oil; this was measured for a number of concentrations by the drop method just discussed, and the σ—c curve plotted (Fig. 9). The rest of the procedure will be best illustrated by an actual numerical example. Five hundred cubic centimetres of a solution containing approximately ·33% of the salt was shaken with ·447 c.c. of oil for 12 hours to form an emulsion. A number of the oil globules thus formed were measured by the microscope, and the average radius found to be 425×10^{-7} cms. From this it is possible to calculate the surface, $4\pi r^2$, and the volume, $\frac{4}{3}\pi r^3$, of a drop. The number of drops is accordingly the total volume of oil used divided by the volume of one drop :—

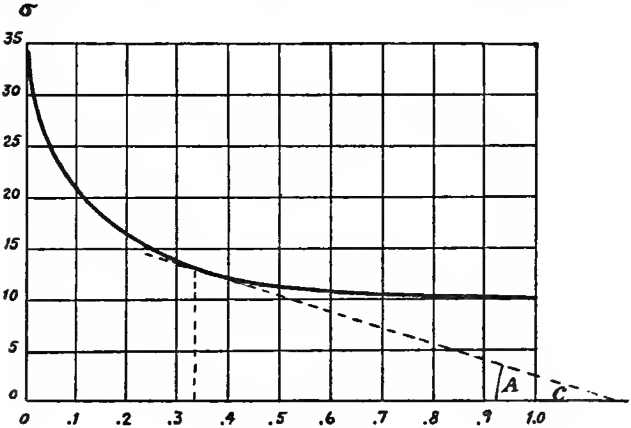

FIG. 9.

$$N = \frac{·447}{\frac{4}{3}\pi r^3}$$

The total surface of oil in contact with the solution is the number N, of drops, multiplied by the surface of one drop, and was found to be 31,553 sq. cms.

After allowing the emulsion to stand for a time the drop number was taken, the assumption being made that the oil globules would have no effect. The figures were :—

Before emulsification :
Drop number = 483 $\sigma = 12{\cdot}8$ $c = {\cdot}318\%$
After emulsification :
Drop number = 459 $\sigma = 13{\cdot}4$ $c = {\cdot}295\%$

The change in concentration, therefore, amounts to ·023 %, so that the total amount removed from the solution by adsorption on the surface of the oil drops is ·115 gm. Hence the amount adsorbed per square centimetre—u in the formula—is this weight divided by the surface of oil :—

$$u = \frac{{\cdot}115}{31{,}553} = 3{\cdot}6 \times 10^{-6}$$

It is also possible to calculate u from the formula, as the values of R, θ and c are known, and the value of $\frac{d\sigma}{dc}$ can be obtained from the σ—c curve (Fig. 9). If the tangent to the curve is drawn at the point having $c = {\cdot}318\%$ as abscissa, the trigonometrical tangent of the angle A is $\frac{d\sigma}{dc}$.

A serious discrepancy was found between the experimental and the calculated values of u, the former being 20—30 times greater than the latter. This is no doubt due in part to the experimental errors involved in the method, inasmuch as the size of the oil globules in the emulsion varies considerably and it is therefore difficult to obtain a reliable value for the radius, and consequently for the total active surface.

The experiment was therefore varied by allowing the oil to rise through the solution in very fine drops of definite size. The change in concentration was again measured by taking the drop number before and after treatment with a known number of drops. The principle of this altered method will be easily understood from a description of the apparatus used in a third series of experiments, in which mercury in the form of fine drops was used as the adsorbent (Fig. 10).

A solution was placed in the vessel, CDE, and drops of mercury from A and B allowed to fall through the solution for some hours, the head of mercury being maintained nearly constant. The mercury collected in E and, as the drops coalesced, the surface was reduced and the adsorbed substance liberated. The constriction at F was provided to prevent diffusion of this released substance backwards into C. It was found that the equilibrium was attained, *i.e.*, that the drops had adsorbed the maximum amount of solute, if they took about six seconds

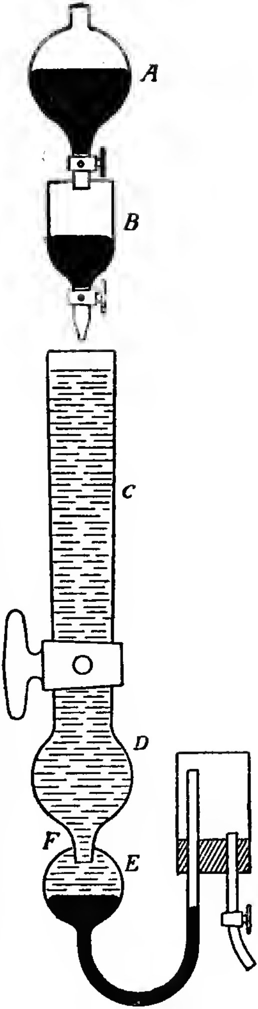

FIG. 10.

to reach F. As in the previous experiment, it was necessary to know the size of the drops to permit calculation of the total adsorbing surface. To accomplish this, a greased plate was moved rapidly across the mercury jet just above the level of the solution in C, and the drops were thus kept separate and could be counted. A number of drops were collected, cleaned and weighed; from this total the weight of one drop, and consequently its volume and surface area, could be calculated. In carrying out an adsorption experiment, the total weight of mercury which had passed through the solution was also determined; its volume divided by the known volume of one drop gave the number, N, of drops, and N × (surface of one drop) was accordingly the total adsorbing surface. To find the concentration of the solution in C before and after adsorption, surface tension measurements by the drop method were again employed. The rest of the procedure was as previously described, viz., a σ—c curve was determined, from which the concentration of the solution for a given c, and the value of $\frac{d\sigma}{dc}$ for a given c, could be taken directly.

The results obtained with various solutions show that dissolved substances can be divided into three classes:—

(1) Those of complex constitution and high molecular weight, *e.g.*, sodium glycocholate, Congo red, methyl orange, sodium oleate, which show adsorption 20—100 times larger than that calculated from the formula.

(2) Simpler compounds, like $AgNO_3$, KCl, $BaCl_2$, $CuCl_2$, which show adsorption 5—10 larger than the theoretical figure (these cases may be complicated by dissociation and ionic adsorption, which will be referred to later).

(3) Caffeine and aniline, which show practical agreement with theory.

It must be added that in the class (2), and still more in (3), the excess *u* was so small that very little reliance can be placed on the experimental figures.

In view of the fundamental importance of the Gibbs-Thomson formula, and the magnitude of the discrepancies between the figures calculated from it and the experimental results, it is of obvious interest to inquire to what causes the deviations may be due. The first point to be noticed is that the complex substances which exhibit them most markedly form, at least at higher concentrations, colloidal and not true solutions. It is, therefore, very probable that they may form gelatinous or semi-solid skins on the adsorbent surface, in which the concentration may be very great. There is a considerable amount of evidence to support this view. Thus Lewis finds that, if the thickness of the surface layer be taken as equal to the radius of molecular attraction, say 2×10^{-7} cms., and the concentration calculated from the observed adsorption, it is found, for instance, for methyl orange, to be about 39%, whereas the solubility of the substance is only about ·078%. The surface layer, therefore, cannot possibly consist of a more concentrated solution of the dye, which is the only case that can be dealt with theoretically, but must be formed of a semi-solid deposit.

A large number of the dyes which behave abnormally when adsorbed exhibit photo-electric properties in the *solid* state, *i.e.*, they emit negatively charged particles when illuminated with ultra-violet light. Adsorbed layers of these dyes show a similar behaviour and are therefore probably composed of solid substance.

The existence of semi-solid pellicles or membranes on the surface liquid-air has also been proved for a number of substances other than dyes, *e.g.*, for albumin by Ramsden, for peptones by Metcalfe, and for saponins by Shorter. In forming these the substance may even be profoundly modified—thus the albumin becomes insoluble when adsorbed in the surface.

The explanation just suggested does not apply to substances which are very soluble and which are in true solution at all concentrations. There is, however, the possibility that the Gibbs-Thomson formula may only be approximate even for such solutes. When we examine the method of derivation of the formula, we find the assumption made that the energy of the molecules of solvent in the surface layer is not altered by the adsorption, *i.e.*, by the increased concentration of molecules of solute. But we have seen before that when a solution and its solvent are separated by a semi-permeable piston, a motion of the latter takes place; this proves that the energy of the molecules of solvent on the two sides of the membrane is different. A further possible source of error is the alteration of the compressibility of the liquid forming the surface layer. Owing to the high concentrations which may occur in this layer, such a change is probable, since the compressibility of solutions is lower than that of the solvent. But we know from a previous chapter that a lower compressibility means a higher intrinsic pressure, *i.e.*, a greater mutual attraction between the molecules, and we also know that various other properties of a liquid alter with its intrinsic pressure. In Gibbs' method of obtaining the adsorption formula all these changes and their possible effect on the balance of energy are neglected, and it is, therefore, quite possible that the formula may be inaccurate, although it is very difficult to estimate the magnitude of the error involved.

On the other hand, the experimental tests of the adsorption formula so far described are not free from objections. From what has been said, it will be clear that the dissolved substance, if it is to afford an accurate test, must fulfil the following conditions:—

(1) It must be of simple and definite chemical constitution and form true aqueous solutions of simple and definite character;

(2) It must be non-volatile and sufficiently soluble in water under the conditions of the experiment; and

(3) It must cause a large decrease of surface tension even in extremely dilute solution.

In Lewis's experiments, although they are extremely ingenious and suggestive, most of the substances employed do not fulfil condition (1). In others, although the discrepancy between calculated and observed results is not considerable, there is a large margin of possible error on account of condition (3) being unsatisfied. Thus, with aniline the change in drop number caused by adsorption was only 1 in 465.

The sources of error indicated above were avoided in a series of experiments carried out by Donnan and Barker, which in principle resemble those made by Lewis, so that only a brief reference to them is necessary. The dissolved substance was nonylic acid, and a $\sigma - c$ curve was plotted by using the drop method. The results could be reproduced with very great accuracy, *i.e.*, to a fraction of one drop in 300—500 drops. Adsorption was produced at a surface air-liquid, air being passed through the solution in bubbles of known size and number, so that the total active surface could be calculated. The bubbles, on reaching the surface, burst, hence the excess of solute carried by them remained in the surface; very effective precautions were used to prevent diffusion backwards from this portion into the bulk of the solution. With a solution containing ·00243 % the excess per square centimetre of surface was found to be $·95 \times 10^{-7}$ gm., while the excess calculated from the Gibbs formula was $·55 \times 10^{-7}$ gm.

Considering the difficulties of the experiments, Donnan and Barker conclude that they may be held to verify the formula.

The investigations described in the preceding pages have been directed to one point only: the exact determination of the excess of dissolved substance in the surface layer at one particular concentration. There are, however, some further questions of great importance, the answers to which must be sought by other experimental methods. The first of these is: does adsorption lead to a well-defined equilibrium in a short space of time? the second: is this equilibrium, assuming it to exist, a simple function of the concentration?

It will be obvious from the description of Lewis's and Donnan and Barker's experiments that equilibrium is assumed to establish itself during the time of contact between the mercury or air surface and the liquid; in fact this point was checked by increasing the time and showing that the result was not affected, *i.e.*, that no further quantity of the solute was removed from solution. Experiments to decide this question had, however, been made at an earlier date by Wilhelm Ostwald. The strict definition of an equilibrium requires that it should be independent of the mass of the phases in contact; thus, a soluble substance and its concentrated solution are in equilibrium at a given temperature and pressure, and this obviously remains unaffected by altering the quantity of either solid substance or solution. Ostwald placed a quantity of charcoal in a given volume of dilute hydrochloric acid and determined the decrease in concentration after a short time. If, then, a part of either the charcoal or the dilute solution was removed, the concentration of the latter remained unaltered, which showed that a state of equilibrium had been established.

The subsidiary question, how long this state takes to establish itself, is not nearly so easily settled, and recent investigations in particular go to prove that very complicated conditions may arise. It has been assumed—tacitly in the experiments so far described, explicitly by Freundlich and others, whose work we shall discuss below—that the time required to establish equilibrium is very short. This is no doubt true in many instances, but numerous combinations of adsorbents and solutes are known in which the first rapid change in concentration is followed by a further, quite continuous, prolonged, and by no means negligible disappearance of solute from the solution. Among the most recent results of the kind may be quoted those of v. Georgievics, who uses wool as adsorbent, and finds that equilibrium is not reached in solutions of acids and dye-stuffs in several days.

It is, of course, possible to suggest various explanations of these observations, the following being most generally accepted :—

(1) The external surface of such porous bodies as charcoal, which is in immediate contact with the liquid, adsorbs very rapidly. The internal surface, however, *i.e.*, that of the pores, can only get its supply of solute by diffusion, which is necessarily slow through the very restricted sections, and particularly so with substances of high molecular weight.

(2) The solute concentrated on the surface may form a solid solution with the adsorbent, which would necessarily be a slow process too.

(3) Chemical action between the highly concentrated solute and the adsorbent may occur. This explanation cannot be rejected *à priori* even in cases where it appears extremely improbable. Thus

it is fairly definitely established that oxidation of carbon takes place when potassium permanganate is adsorbed by charcoal.

Of course all these phenomena, if or when they occur, are distinct from and consequent on adsorption in the narrow sense of the term. At the same time, they render the selection of a point at which adsorption is complete and secondary phenomena begin at least arbitrary and tend to obscure the question of adsorption equilibrium.

On the other hand, in a sufficient number of cases a definite equilibrium is undoubtedly reached in a short time, and if we confine ourselves to these, it becomes possible to approach the second question we have put, that referring to the connection between concentration and amount adsorbed. Among the investigators who have treated this problem both mathematically and experimentally Freundlich deserves to be mentioned particularly.

We cannot give even an outline of the mathematical treatment, and must confine ourselves to stating the result in the symbols usually employed, although the choice of these is not altogether happy from the point of view of mathematical clearness and elegance.

If we call—

x the amount adsorbed,
m the quantity of adsorbent in grammes,
C the concentration in the solution after adsorption, *i.e.*, the equilibrium concentration,
a and n constants (where $n > 1$) for a given solute and adsorbent,

the following relation exists between these :—

$$\frac{x}{m} = aC^{\frac{1}{n}}$$

It must be borne in mind that the two variables in this formula are x and C, and that the latter is the equilibrium or end concentration after adsorption. The formula, therefore, does not enable us to calculate beforehand what amount of solute will be adsorbed by an amount m of adsorbent.

The formula is very frequently referred to, in chemical and biological literature, as an " exponential " one. This is an error which deserves to be pointed out, as the title belongs properly only to functions in which one of the variables—in our case x and C—appears as exponent, and as such true exponential functions have very peculiar properties. In the adsorption formula the exponent $\frac{1}{n}$ is a constant, and the equation is, therefore, that of a general parabola. If we make $n = 2$, a case which actually occurs, the formula becomes

$$\frac{x}{m} = aC^{\frac{1}{2}}$$

or, in a more familiar form,

$$x = am\sqrt{C}$$

which is the equation of the ordinary parabola.

Another form of the equation is even simpler, and is particularly useful in representing experimental results. If we take the logarithms on both sides, we obtain

$$\log x - \log m = \frac{\log C}{n} + \log a$$

In this equation the variables are log x and log C. Since the expression is linear, the curve obtained by plotting log x and log C as co-ordinates is a straight line.

As the adsorption formula may be stated in the simple terms that the amount adsorbed by the unit quantity of adsorbent is proportional to the nth root of the equilibrium concentration, it is obvious that it increases with, but much more slowly than, the latter. No maximum adsorption at any particular concentration is, therefore, possible in normal cases, but a number of anomalous instances have been observed in which such a maximum occurs; in other words, the phenomenon does not follow the simple course expressed by the parabolic curve.

The experimental verification of the adsorption equation is comparatively simple, apart from certain experimental difficulties. Solutions of different known concentrations are prepared and equal amounts of adsorbent are placed in equal volumes of these solutions. Agitation of some sort is generally necessary to ensure complete adsorption. When equilibrium has been reached, the concentrations of the various solutions are again determined and represent, of course, the end or equilibrium concentrations, viz., the values of C in the formula. The differences between these and the original concentrations are the amounts adsorbed, that is, the x or $\frac{x}{m}$ in the formula—the latter, as we are at liberty to choose the (equal) amounts of adsorbent as unity. The values so obtained can then be plotted; as it is, however, not quite easy to determine the character of the curve, the principal feature of which is the constancy of the exponent $\frac{1}{n}$, it is preferable to plot the log x—log C curve, which must be a straight line if the adsorption formula holds good.

Although the experimental technique is quite simple, it presents certain difficulties. Among these the principal one is that of obtaining concordant results with different portions of the same adsorbent. The only possible method is to use equal weights, whereas what is really required is equal surface, and even with apparently uniform substances like blood charcoal it is not certain that equal weights really have equal surfaces. The selection of suitable solutes also requires care; since very low concentrations have to be determined with high accuracy, substances must be chosen which lend themselves to such determinations. From what has been said earlier, it is obvious that complications arise in solutions of electrolytes—to which we shall refer again—and it is, therefore, necessary, in testing the formula, to select non-electrolytes, or at least substances which are very slightly dissociated.

A large amount of material has been collected, especially by Freundlich, and Fig. 11 shows two very typical adsorption curves obtained by him. Fig. 12 gives the corresponding log x—log C diagrams, which show a very good approximation to straight lines. The adsorbent in both cases was blood charcoal; the solution for A was benzoic acid in benzene, for B succinic acid in water. The characteristic feature of each curve is, of course, the exponent $\frac{1}{n}$, and it is, therefore, of interest to compare the exponents for various substances. A number of these, also determined by Freundlich, are given in the following table; the adsorbent in all cases was blood charcoal the solvent, unless otherwise stated, water:—

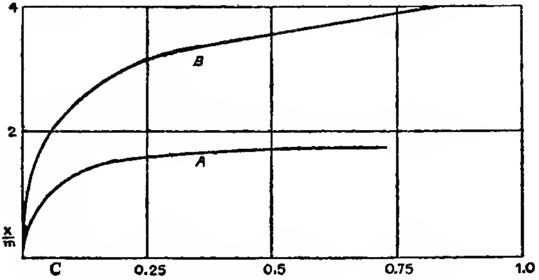

FIG. 11.

	$\frac{1}{n}$.
Formic acid	·451
Acetic acid	·425
Propionic acid	·394
Butyric acid	·301
Monochloracetic acid	·363
Succinic acid	·243
Benzoic acid	·338
Chlorine	·297
Bromine	·340
Picric acid in alcohol	·230
Benzoic acid in benzene	·416
Bromine in ether	·263

With certain dye-stuffs in water the exponent becomes as low as ·19 to ·11. Generally speaking, it lies between these figures as lower and ·5 as upper limit.

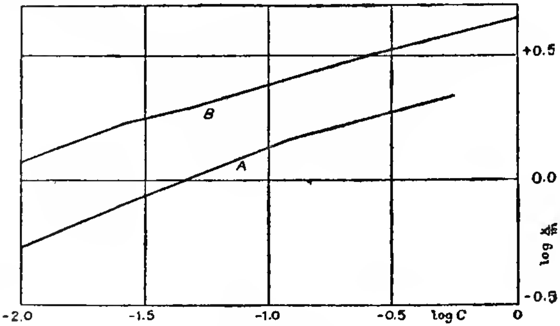

FIG. 12.

It is of interest to examine how adsorption, for one and the same substance, is affected by the adsorbent and by the solvent. As regards the former, any comparison is difficult, owing to the impossibility of determining even approximately the active surfaces in the case of two different substances like, say, charcoal and silk fibre. Leaving absolute quantities out of consideration, experiment shows that the order in which several solutes are adsorbed by different adsorbents is the same, *i.e.*, if a substance, A, is more strongly adsorbed by charcoal than B, and this again more strongly than C, the same order will hold good if another adsorbent is used, although the numerical ratios may be different.

As regards the solvent, it is obvious on theoretical grounds that this must have a marked effect, depending chiefly on its surface tension. The increased surface concentration is the result of the lowering of the surface tension by the solute, and it is only reasonable to assume that this lowering will be more marked in a solvent with high surface tension, like water, than in solvents with lower surface tension, like the organic solvents. We should, therefore, expect adsorption to be greater in aqueous than in organic solutions of the same substance and of equal concentrations, and this view is entirely borne out by experiment. The following figures show the relative amounts adsorbed by charcoal from solutions of equal concentration in different solvents :—

Benzoic acid	in	water	3·27
,,	,,	benzene ..	·54
,,	,,	ether	·30
,,	,,	acetone ..	·30

The surface tensions of the solvents are respectively, 75, 29, 16, and 23.

The different rate of adsorption in aqueous and alcoholic solution can be demonstrated by a simple experiment. Charcoal in sufficient amount is shaken with a dilute aqueous solution of crystal violet and renders the solution practically colourless. If the latter is now replaced by an equal volume of alcohol, this becomes deeply coloured. The explanation is simple: the adsorbed amount in equilibrium with the bleached aqueous solution is much greater than the amount which would be in equilibrium with an equally weak alcoholic solution, and a portion of it, therefore, becomes redissolved, leaving a smaller surface concentration in equilibrium with the solution.

CHAPTER V.

It has been shown in the preceding chapter that the distribution of the solute particles in a solution depends, not only on the surface tension, but also on the electrical charges which may exist on the particles. This factor will have especial weight in the case of electrolytes, where the ions are known to be charged, and certain effects of surface tension may be seriously modified, if not altogether masked. It is to the consideration of these electro-capillary effects that we now turn our attention. To form a mental picture of the electric field it is convenient to follow a method originated by Faraday and now used by all physicists. If a charged body is held near an oppositely charged or electrically neutral body mutual attraction occurs, exactly as if the two were connected by tense elastic threads. Faraday supposed that imaginary lines, in a state of tension, connected oppositely charged points; these he called lines of force. Many properties of electric charges can be foretold if it is assumed: (1) that the lines of force are in a state of tension; (2) that they repel each other sideways. Thus if a charge is put on a metal sphere at A (Fig. 13), lines of force are concentrated on this point, but, owing to their mutual repulsion, they spread sideways until all the pressures are equal, and the charge is uniformly distributed over

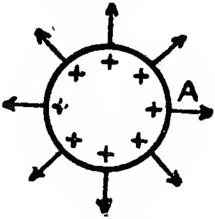

FIG. 13.

the surface. As the lines are in a state of tension, it is clear from the figure that the sphere will tend to expand on account of the outward pull. If the sphere were a liquid drop, its surface tension would cause it to assume a minimum surface area ; the effect of the electric charge is to oppose this, and the net result is that *the liquid behaves as if it had a reduced surface tension.*

This result introduces important modifications when a saturated vapour is condensing into liquid drops. Surface tension, as has been shown in Chapter II., makes the initial stages of condensation more difficult ; but if it can be arranged that the droplets form on a small electrically charged body, the deterrent effect of the surface tension can be greatly reduced and condensation is accelerated. This has been beautifully shown by C. T. R. Wilson in a series of experiments. Air, saturated with water vapour, was confined in a bulb and, by means of a piston arrangement, it could be made to expand suddenly ; the temperature therefore fell and liquid condensed on any dust particles that happened to be present. The fog so produced was allowed to settle, carrying the dust down with it. After several repetitions all the dust was removed and no fog was produced except with large expansions. An X-ray bulb or a small amount of radium was now caused to send rays through the gas. (These are known to produce electrified particles, or ions.) A much smaller expansion now produced a very dense fog. Most vapours condense the more readily on positively charged ions ; water forms the chief, if not the only, exception to this rule.

The presence of gaseous ions will make it difficult to dry a gas thoroughly. This is perhaps best seen from energy considerations. If Q is the charge on a drop of liquid of radius R, the electrical energy is $\frac{1}{2}Q^2/R$. As the drop evaporates R diminishes but

Q remains the same, *i.e.*, evaporation increases the electrical energy; hence the presence of the charge makes evaporation more difficult. Surface tension, as we have seen in Chapter II., promotes it. At some stage of the process there will be equilibrium between the two effects and the drop will persist. Owing to the universal distribution of radioactive substances gaseous ions are always being produced in the atmosphere, and moisture condenses on them. Once formed, the drops persist, with a radius of about 3×10^{-7} cms. at room temperature. To reduce the radius by one-half by evaporation, it has been calculated by Sir J. J. Thomson that the surrounding air must be dried so completely that the moisture present is only 3×10^{-16} of that required to saturate it. Professor Baker has demonstrated the efficiency of moisture in promoting chemical reactions; the figures just quoted show the difficulty of securing perfect dryness. Apparently the last stages of drying are due, not to the removal of gaseous water vapour, but rather to the entanglement of the more persistent drops in the drying agent. If this is really so, the final traces of moisture could be more quickly removed by placing the gas in an electric field, and so driving the charged drops on to the absorbent!

In emulsification a large amount of surface energy is produced owing to the great surface area of the disperse phase; the emulsion is more easily produced if this energy is reduced by the employment, as continuous phase, of a liquid having a low surface tension, like soap solution. The lowering of the effective surface tension by the electric charges, usually present on the small drops, will also assist the process. The increased stability of an emulsion or a suspension due to these charges has already been mentioned.

The effect of electrification on surface tension can be directly measured by means of the capillary electrometer (Fig. 14). A glass tube A, drawn out below to a fine conical capillary, is connected by rubber tubing to a movable reservoir; each contains mercury. The capillary dips into a solution of electrolyte, below which is a further layer of mercury. The mercury surface in the narrow tube is very convex downwards, and, owing to the surface tension mercury-electrolyte, can support a pressure $2\sigma/a$, σ being the interfacial tension, and a the radius of the tube at the given point (Chapter II.). If σ is increased the equilibrium is disturbed and a larger head of mercury must be employed to keep the meniscus at the same level. The length of the mercury column in A is evidently proportional, in these conditions, to the interfacial tension mercury-electrolyte. The mercury side of this surface can be charged with negative electricity by the device shown in the figure. A current is

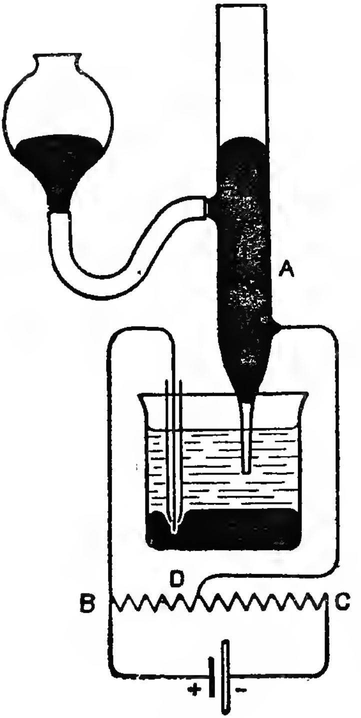

FIG. 14.

sent from a battery through a thin wire BC, the positive pole being joined to B. This point is also connected to the mercury at the bottom of the beaker. A wire D, sliding along BC, is connected to the mercury in A. As D is moved from B to C it is clear that the mercury meniscus receives a larger negative charge from the negative pole of the cell, the corresponding positive charge moving upwards through the electrolyte from the other pole. An increasing potential difference is thus established across the mercury-electrolyte surface, until the

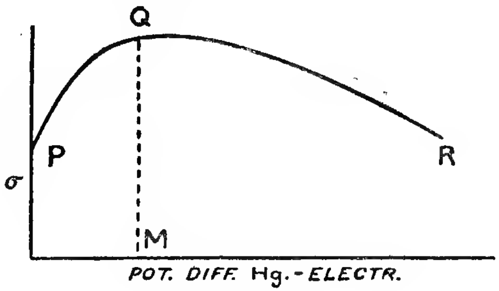

FIG. 15.

resistance is broken down, current passes, and electrolysis begins. The surface tension corresponding to any potential difference is measured in arbitrary units, by the height of the column in A. The curve in Fig. 15 shows how σ depends on the potential difference between the mercury and electrolyte. It reveals, at least, one unexpected feature. Since an electric charge apparently lowers the surface tension, we should expect a gradual decrease as the potential difference increases, while, in fact, σ first increases to a maximum before finally diminishing. The maximum at Q corresponds to a potential difference between B, D of 0·926 volt for Hg — normal

H_2SO_4. Either previous ideas of the influence of a charge on surface tension must be revised, or a new factor must be looked for. Helmholtz adopts the second alternative. He supposes that there is a double layer of electricity at the mercury-electrolyte surface under normal conditions, the mercury being positively and the adjoining layer of electrolyte negatively charged.

Evidence in favour of such a double layer can be gathered from other, purely electrical, phenomena. Hence at the beginning of the experiment, corresponding to the point P on the curve, we are dealing not simply with the interfacial tension Hg — electrolyte but with a tension modified by the presence of this double layer of electricity. If σ is the surface tension when there is no charge, then, holding to our previous views, the tension, when a double layer is present, is less than σ. As the mercury is supposed to have a positive charge initially, the effect of giving it a negative one is to annul partially this primary charge and so to increase σ, until, at Q, the surface is electrically neutral and the tension has its highest value. Beyond this point, as the potential between B, D is further increased the mercury becomes negatively charged, a new double layer is created in the reverse direction, and σ decreases in the usual way.

When there is no double layer present—corresponding to Q according to Helmholtz—the liquids are said to be iso-electric. This condition possesses considerable chemical interest in connection with the coagulation of precipitates or of bacteria. A finely divided precipitate is the seat of considerable surface energy; coagulation reduces this by decreasing the surface area, and the reduction is all the more pronounced the greater the interfacial tension. Hence a large surface tension promotes coagulation, and should therefore be most efficient at the iso-electric point. As the position of this point can be altered by suitable additions of acid or alkali, it should be possible to attain the best conditions for the purpose.

There is considerable evidence that whenever two immiscible substances are brought together a double layer at the interface results, but recent work has made it doubtful whether, in every case, the iso-electric point corresponds with the condition of maximum surface tension.

It is an interesting question whether the effects just described are different for the anions and kations. The Helmholtz theory neglects this factor and ascribes them entirely to the stresses in the lines of force, independently of the direction of the latter. If this were true, starting with the surfaces uncharged (as at Q), equal positive or negative charges on the mercury should lower the surface tension by the same amounts, and the curve PQR should be symmetrical round Q. Experiment shows that this is not the case, but the branch PQ is steeper than QR. There is therefore a specific action depending on the nature of the ion. Along PQ the electrolyte surface is negatively charged, according to the Helmholtz theory of the initial double layer (*vide supra*), that is the anions are more effective than the kations in lowering the surface tension. Van Laar has revised Helmholtz's calculations, taking into account this new effect, and finds excellent agreement with the measurements of S. W. J. Smith. These experiments are given later.

As regards the origin of the double layer the Helmholtz theory gives no information, but several other theories have been formulated. Modern electrical theories suppose every conducting substance to contain large numbers of negatively charged ions, called electrons, which are exactly alike no matter in what substance they are found. When two substances, containing different numbers of electrons, are brought together, there is a redistribution between the two ; that body which loses negative electricity, of course, becomes positively charged, while the other becomes negative. This would account qualitatively for the layer, but the theory is insufficiently developed to make possible a quantitative test. The double layer is evidently due to selective adsorption of the ions ; in the case we have considered it is the negatively charged ion that is most readily abstracted from the electrolyte. The object of any theory must be to explain why this selective adsorption takes place.

Another theory which has given rise to much research is due to Nernst. As it is closely connected with the question of the iso-electric point it must be considered briefly. When a solid like zinc is placed in a liquid, Nernst supposes there is a pressure, of the nature of an osmotic pressure, tending to force the zinc ions into solution. This he calls the solution pressure. Zinc being electro-positive, its ions are positively charged ; the liquid thus becomes positively and the zinc, on account of its loss of positive ions, becomes negatively charged. A difference of potential between solid and liquid is thus created, and, as the ions are attracted to the negatively charged zinc, a double layer is formed at the interface. When zinc ions are already in the liquid they may be deposited on the zinc instead of more going into solution. If these effects take an appreciable time to establish themselves, it should be possible, by tests made immediately after the contact of solid and liquid, to get rid of the influence of the double layer, and zinc and liquid would then be at the same potential. This is the principle of the dropping electrode in which the zinc is replaced by mercury. Suppose, for example, in the capillary electrometer (Fig. 14) that the mercury falls out of tube A in a fine jet, which breaks into drops before the double layer is formed. Mercury and solution are then at the same potential, but the double layer is formed as usual over the mercury at the bottom of the beaker. Hence if the potential difference is measured between the mercury in the funnel and that below the solution, there would be found the potential difference across this double layer. This should equal the potential difference required to produce the maximum surface tension when the electrometer is used in the ordinary method already described. This is found to be the case if the jet is in air and breaks into drops in the surface of the liquid. It would thus appear that from observations of surface tension there can be found the difference of potential between mercury and electrolyte, the required result being the E.M.F. at which the surface tension is a maximum. S. W. J. Smith's experiments show that this is not generally true, and that the potential difference between mercury and electrolyte is not necessarily zero when the surface tension is a maximum. This result is of particular interest in view of the importance assigned to the iso-electric point in the theory of coagulation of suspensions, which has already been pointed out.

If solutions of two electrolytes are brought into contact there is, generally speaking, a potential difference between them, just as there is one at the interface mercury-electrolyte in the capillary electrometer. This potential difference has been shown by Nernst to depend on the differences in the concentrations and the migration velocities of the ions. Smith uses dilute solutions containing equivalent amounts of KI and KCl; the kation is thus the same in both solutions, and the migration velocities of the I and Cl ions are nearly equal, so that, according to Nernst's theory, there should be no potential difference or double layer at the interface. These two solutions were employed in the following three experiments :—

(1) Surface tension-potential difference curves for each electrolyte against mercury are plotted in the capillary electrometer, the result being shown in Fig. 16. At P there is, according to Helmholtz, no potential difference between Hg – KCl, and at R none between Hg — KI. If the effects at the interface were purely electrostatic, *i.e.*, dependent only on the lines of force, and if the anions had no specific influence, then QS should be zero. Actually, however, it represents a potential difference of 0·2 volt.

(2) The potential difference between Hg — $\frac{n}{10}$KCl, and also that between Hg — $\frac{n}{10}$ KI is measured by the capillary electrometer or by a dropping electrode (these correspond to OQ, OS in Fig. 16). A cell is now made up consisting of Hg – $\frac{n}{10}$ KCl $\frac{n}{10}$ KI – Hg, as shown in Fig. 17, platinum wires being fused in to make contacts with the mercury. The E.M.F. of such a cell, according to Nernst's theory mentioned above, is the algebraic sum of the potential differences across the double layers occurring at the surfaces of contact between different substances. This E.M.F. can readily be measured by the usual electrical methods. As regards the various potential differences of which it is the algebraic sum, those between the platinum electrodes and the mercury cancel each other, since they are equal and opposed ; that at the interface KCl – KI is zero, as explained under (1) ; hence the E.M.F. should be the algebraic sum of, or difference between, the potential differences arising at the interfaces Hg — KCl and Hg — KI. If the anion had no specific influence, this should be zero : actually it is about 0·2 volt, in agreement with the results obtained above. This

shows clearly that the potential difference at an interface mercury-electrolyte depends, not only on the lines of force, but also on the chemical nature of the ions forming the double layer.

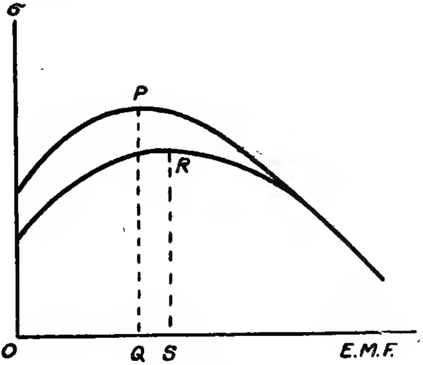

FIG. 16.

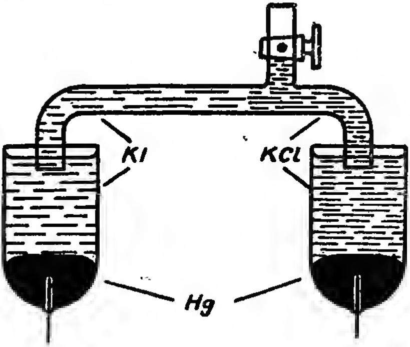

FIG. 17.

(3) In order to produce the maximum interfacial tension in a capillary electrometer, it is generally necessary to apply a polarising E.M.F. Palmaer

and Smith have, however, made solutions for which the maximum tension occurs when the applied E.M.F. is zero, in which case the points P and R of the curve shown in Fig. 16 fall on the axis Oσ. Such solutions are called " null solutions," and, according to Helmholtz's theory, must be taken to possess the property that there is no double layer and no potential difference between mercury and such a null solution. Smith replaces the decinormal KCl and KI solutions in the cell of Fig. 17 by two different null solutions so chosen that there is no potential difference at their interface. The E.M.F. of such a cell should then be zero ; it is found, however, that this is not the case and that the anion again has a specific effect on the mercury surface.

As a result of these experiments Smith concludes that (*a*) the simple Helmholtz theory of the double layer is insufficient to account for all the observed facts. The potential difference mercury-electrolyte is not purely electrostatic, but depends on the nature of the ions, as, according to Nernst's theory, it should do. This theory, it will be remembered, involves the " solution pressure " of the ions, which varies with their chemical nature. (*b*) The potential difference mercury-electrolyte is not necessarily zero when the interfacial tension is a maximum, although in the particular case of dilute KCl this condition is very nearly fulfilled.

In our discussion of the Gibbs-Thomson formula, it was pointed out that the presence of an electric charge on the particles of adsorbed substance might considerably affect the amount adsorbed. We now proceed to give some attention to this point, in the light of what has been established in the preceding pages concerning the interaction between surface tension and electric charges. To take a simple case, we will examine what may be expected to occur, according to Nernst's solution pressure theory, when drops of mercury are allowed to fall through a solution of Hg_2SO_4. The solution pressure, P, of mercury is very small and is lower than the osmotic pressure, p, of the mercurous ions in solution. Hence these ions will be deposited on the mercury surface and will by their positive charge attract SO_4 ions, thus forming a double layer. Hg_2SO_4 will accordingly be abstracted from the upper layers of the solution and will be carried downward by the drops, to be set free again when they coalesce—with consequent decrease of surface—at the bottom of the vessel. This change in concentration has actually been observed by Palmaer, and was, in fact, what enabled him to discover when his solutions were "null solutions." But this is just what would be expected if the whole phenomenon were due to adsorption in the strict sense of the term, *i.e.*, to changes in surface concentration caused by a decrease of surface energy, as in the experiments of Lewis and of Donnan and Barker. No change would occur if the solution pressure and the osmotic pressure were equal, or if a null solution were used. These, however, deal practically with non-electrolytes, and, in deriving a formula applicable to the new conditions, account must be taken of the electrical energy of the adsorbed ions. Lewis has carried out the calculation necessary to show how this affects the amount adsorbed. If V is the potential difference across the double layer at the interface Hg − Hg_2SO_4, and a and b the electrochemical equivalents of the negative and positive ions respectively, *i.e.*, the mass of each deposited when unit quantity of electricity is passed through a solution of the electrolyte, the Gibbs-Thomson formula becomes :—

$$\mathrm{U} = u_{\text{salt}} + u_{+} + u_{-} = -\frac{c}{\mathrm{R}\theta}\left[\frac{d\sigma}{dc} + (a+b)\frac{d\sigma}{d\mathrm{V}}\right].$$

a and b are known from electrochemical data, while $\frac{d\sigma}{dV}$ can be found from the σ — E.M.F. curve given by the capillary electrometer, hence the amount adsorbed of each ion can be calculated. In this way Lewis finds :—

$$u_{\text{salt}} = 2{\cdot}7 \times 10 \times 10^{-7} \text{ gms./cm.}$$
$$u_{+} + u_{-} = 3 \times 10^{-8} \text{ gms./cm.}$$

It will be noted that there should be no ionic adsorption when the interfacial tension is a maximum, as at that point a small alteration in V produces no change in σ, *i.e.*, $\frac{d\sigma}{dV} = 0$. The second term in brackets, therefore, becomes $= 0$, and the formula the original Gibbs-Thomson equation.

The question arises whether this absence of ionic adsorption at the point at which the ions do not affect the interfacial tension does not afford the true explanation of the phenomenon ; that is, whether the effect is due to a lowering of interfacial tension, as in the case of non-electrolytes, rather than to the joint action of osmotic and solution pressures. Nernst's theory, although accounting for observed facts, postulates a force—solution pressure—concerning whose origin little, if anything, is known. On the other hand, we are quite ignorant of the effect of ions on surface or interfacial tension, nor does it seem possible to devise any experimental methods for measuring such an effect. Lewis has calculated from Nernst's theory the mass of ions adsorbed, and finds the sum $u_{+} + u_{-} = 1{\cdot}4 \times 10^{-7}$ gms./cm. The order is not very different from that of the figure obtained above from the modified Gibbs-Thomson formula, but some of the numerical data on which Lewis's calculation is based are open to question.

What has been developed in the preceding paragraphs as to the nature and probable origin of the double layer has a most important bearing on colloidal chemistry. As is well known, the electrical behaviour of at least one class of colloids, the suspensoids, is among their most characteristic properties, but the origin of the electric charge on colloidal particles is, of course, as uncertain as that of the double layer in the capillary electrometer. Opinion now generally inclines to the view that it is not electrostatic, but due to adsorbed ions; that the latter have specific differences appears strikingly in the cognate phenomenon of electrolyte coagulation, where, *e.g.*, the hydrogen ion in the majority of cases has a much greater effect than the equivalent amounts of monovalent metallic ions. In interpreting these complicated phenomena we are confronted with the difficulty mentioned above—our ignorance of the laws governing the adsorption of ions—and the general difficulty of all adsorption phenomena on solid surfaces. The latter are supposed to be due to reduced surface energy, but we have no means of measuring surface tensions solid-liquid, and can, therefore, only assume that their behaviour for a given solution is parallel to that of liquid-liquid or liquid-gas surfaces, an assumption inherently incapable of proof.

It would therefore be of obvious importance to study the electrical behaviour of a surface liquid-air, since in that case we can determine changes in surface tension directly. Such experiments were already carried out by Quincke, who examined under the microscope the travel of a small air bubble in capillary filled with liquid, in an electric field. The method is therefore substantially cataphoresis, but has the drawback that there is only a minute thickness of liquid between the air surface and the glass wall, and that the portion of liquid film adjacent to the latter also travels in the electric field. Quincke found that air bubbles in water were negatively charged—as are the majority of solids—but that they showed no charge in turpentine. This would point to the ionic origin of the charge, since the latter liquid forms no ions.

An entirely different method for investigating the double layer at a liquid-gas surface is that used by Lenard, Sir J. J. Thomson and others, and known as "waterfall electrification." Drops of liquid are allowed to fall through the gas and impinge on an obstacle; in falling they acquire a double layer, which is supposed to be mechanically separated by the shock of impact, so that the signs of the charges on the liquid and on the gas can be determined. Air in this case becomes—as in Quincke's experiment—negatively charged, the water being, of course, positive. In hydrogen, however, the charges were reversed. Dissolved salts also reversed the charges on water, some dyestuffs in particular showing this effect in extremely minute concentrations. Thus Rohde found that a concentration of 0·1 mg. of fuchsin per litre was sufficient to render the water positive.

It is, however, by no means certain that the results obtained by this method are comparable with those obtained by cataphoresis, or, in other words, that the origin of the double layer is the same in both cases. Thus, in experiments according to Quincke's method made by one of the authors, fuchsin did not reverse the charge on the air bubble even in concentrations a thousand times greater than those found effective by Rohde. Similarly discordant and very important results are obtained by McTaggart, who investigates the cataphoresis of a gas bubble by an improved method. The bubble is placed in the axis of a wide rotating tube filled with liquid and is therefore as freely movable as the particles in the U-tube employed for examining colloidal solutions. He finds that air bubbles are negatively charged in distilled water and travel with a velocity, independent of their size within limits, of about 4×10^{-4} cms. per second in a field of 1 volt/cm. This is in very good agreement with the behaviour of colloidal particles in the same conditions. On the other hand, he finds that in this arrangement hydrogen bubbles are, like air, negatively charged, whereas in waterfall experiments this gas is positive against water. The effect of various cations was found to be similar to that on colloidal particles, ions of high valency having a much greater effect in neutralising and eventually reversing the charge on the bubble, while exhibiting —as in their action on sols—specific peculiarities.

In a further series of experiments McTaggart investigated the electric state of the air bubble in mixtures of water and of several alcohols, and the results obtained are of particular interest, as showing a definite connection between surface tension and electric charge. In the pure alcohols no cataphoresis could be observed. In mixtures of the alcohols and water the velocity of the bubble decreased with increasing alcohol content, and this decrease in velocity — and therefore in electric charge—was the greater the more the alcohol lowered the surface tension of water. The electric charge was therefore reduced by increased adsorption of alcohol at the surface air-solution, and it is reasonable to assume that, with an increased ratio of alcohol in the surface layer, ions would be displaced out of that layer, with a corresponding decrease in the total charge. A further very striking fact was observed : if the size of an air bubble in the water-alcohol mixture was gradually reduced, the velocity, and therefore the charge, increased, approximating more and more to that in pure water. To explain this it is necessary to assume that with decreasing diameter and the consequent change in surface tension the adsorption of alcohol decreases, or, in other words, the percentage of water in the surface layer, and with it that of ions increases. This would be analogous to the change in vapour pressure with the curvature of the surface, which has been fully discussed in a previous chapter.

On the whole McTaggart's experiments, as far as they are at present capable of interpretation, strongly support the view that the double layer is largely or entirely due to the ordinary adsorption of ions.

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